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WATER RENOVATION OF MUNICIPAL EFFLUENTS BY REVERSE OSMOSIS

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Gulf Environmental Systems Company

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16. ABSTRACT

The purpose of the work performed under this contract has been to obtain reverse osmosis operating data on primary and secondary effluents with varying degrees of pretreatment. Field tests were conducted at the Pomona Water Renovation Plant of the County Sanitation Districts of Los Angeles. Two parallel reverse osmosis systems were operated with spiral wound membrane modules.

It was concluded that spiral wound reverse osmosis units can be economically operated on primary and activated-sludge effluents with only moderate pretreatment and periodic chemical cleaning. Activated-carbon pretreatment was shown to be unnecessary for successful operation on sand-filtered activated sludge or chemically clarified and sand-filtered primary effluent. A simplified economic analysis indicated that reverse osmosis treatment costs are favorable and that the process merits serious consideration in a planned water supply and waste management program.

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FOREWARD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report covers work on reverse osmosis of primary and secondary sewage treatment plant effluents with varying degrees of pretreatment. An economic analysis indicated that the process merits serious consideration in a planned water supply and waste management program.

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ABSTRACT

The purpose of the work performed under this contract has been to obtain reverse osmosis operating data on primary and secondary effluents with varying degrees of pretreatment. Field tests were conducted at the Pomona Water Renovation Plant of the County Sanitation Districts of Los Angeles. Two parallel reverse osmosis systems were operated with spiral-wound membrane modules.

Four major field experiments were conducted. In the first, operation on activated-sludge effluent with and without activated-carbon pretreatment was compared. In the second experiment, a comparison was made of different chemical cleaning techniques applied to activated-sludge effluent. In the third experiment, the reverse osmosis units were operated on chemically clarified primary effluent with and without activated-carbon pretreatment. Finally, in the fourth experiment, a reverse osmosis unit was operated on activated-sludge effluent while holding product flow constant to more closely simulate actual plant operation.

It was concluded that spiral-wound reverse osmosis units can be economically operated on primary and activated-sludge effluents with only moderate pretreatment and periodic chemical cleaning. Activated-carbon pretreatment was shown to be unnecessary for successful operation on sand-filtered activated-sludge effluent or chemically clarified, sand-filtered primary effluent. A simplified economic analysis indicated that reverse osmosis treatment costs are favorable and that the process merits serious consideration in a planned water supply and waste management program.

This report was submitted in fulfillment of Project Number 17040EOR, Contract Number 14-12-831, under the sponsorship of the Office of Research and Development, U.S. Environmental Protection Agency.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	5
IV	Cleaning and Pretreatment Technique Development	13
V	Field Tests	42
VI	Economics of Reverse Osmosis Treatment of Sanitary Wastewater	97
VII	References	111
VIII	Patents and Publications	113
IX	Appendices	114
	Technical Report Data	123

FIGURES

		PAGE
1	REVERSE OSMOSIS UNIT FEED STREAMS	11
2	AIR-WATER FLOW DISTRIBUTION TEST RESULTS	36
3	MEMBRANE CHLORINATION TEST FLOW DIAGRAM	39
4	EFFECT OF CHLORINE ADDITION ON MEMBRANE SALT REJECTION CAPABILITY	40
5	EFFECT OF CHLORINE ADDITION ON MEMBRANE WATER PERMEATION	41
6	SCHEMATIC OF POMONA FIELD TEST UNIT	44
7	SCHEMATIC OF EXPERIMENTAL UNIT	46
8	PERCENT SALT REJECTION VERSUS TIME - UNIT I, PHASE V EXTENSION	49
9	PERCENT SALT REJECTION VERSUS TIME - UNIT II, PHASE V EXTENSION	50
10	WATER PERMEATION COEFFICIENT A VERSUS TIME - UNIT I, PHASE V EXTENSION	51
11	WATER PERMEATION COEFFICIENT A VERSUS TIME - UNIT II, PHASE V EXTENSION	52
12	LOADING ARRANGEMENT FOR UNIT I, PHASE V EXTENSION	53
13	PLOTS OF PRODUCT WATER FLUX VERSUS TIME FOR UNITS I AND II, EXPERIMENT I	56
14	UNIT I: CARBON EFFLUENT WATER PERMEATION COEFFICIENT VERSUS TIME - EXPERIMENT I	58
15	UNIT II: SECONDARY EFFLUENT WATER PERMEATION COEFFICIENT VERSUS TIME - EXPERIMENT I	58
16	TOTAL CHEMICAL OXYGEN DEMAND VERSUS TIME FOR UNIT I AND II FEED STREAMS - EXPERIMENT I	59
17	UNIT I AND II FEEDWATER TURBIDITY VERSUS TIME - EXPERIMENT I	61
18	UNIT I AND II SALT REJECTION VERSUS TIME, BASED ON CONDUCTIVITY MEASUREMENTS - EXPERIMENT I	63
19	COMPARISON OF SECONDARY-EFFLUENT-FOULED MEMBRANE WITH CLEAN MEMBRANE SURFACE	65
20	EXPERIMENT II: PERMEATE FLUX VERSUS TIME (550 PSIG FEED PRESSURE)	68
21	UNIT I: SECONDARY EFFLUENT WATER PERMEATION COEFFICIENT VERSUS TIME - EXPERIMENT II	70
22	UNIT II: SECONDARY EFFLUENT WATER PERMEATION COEFFICIENT VERSUS TIME - EXPERIMENT II	70

		PAGE
23	UNITS I AND II: SALT REJECTION VERSUS TIME - EXPERIMENT II	72
24	EXPERIMENT IV: FEED PRESSURE VERSUS TIME	76
25	EXPERIMENT IV: WATER PERMEATION COEFFICIENT VERSUS TIME	77
26	EXPERIMENT IV: LOGARITHMIC PLOT OF WATER PERMEATION COEFFICIENT VERSUS TIME	78
27	EXPERIMENT IV: SALT REJECTION VERSUS TIME	79
28	CARBON-TREATED CHEMICALLY CLARIFIED PRIMARY EFFLUENT: PERMEATE FLUX VERSUS TIME - EXPERIMENT III	84
29	SAND-FILTERED CHEMICALLY CLARIFIED PRIMARY EFFLUENT: PERMEATE FLUX VERSUS TIME - EXPERIMENT III	85
30	CARBON-TREATED CHEMICALLY CLARIFIED PRIMARY EFFLUENT: WATER PERMEATION COEFFICIENT VERSUS TIME - EXPERIMENT III	86
31	CHEMICALLY CLARIFIED PRIMARY EFFLUENT: WATER PERMEATION COEFFICIENT VERSUS TIME - EXPERIMENT III	88
32	UNIT I AND II SALT REJECTION VERSUS TIME - EXPERIMENT III	89
33	EFFECT OF FEED TURBIDITY ON PERMEATION COEFFICIENT DECLINE SLOPE	95
34	EFFECT OF COD ON PERMEATION COEFFICIENT DECLINE SLOPE	95
35	COST OF CHEMICALS FOR CLEANING	98
36	TOTAL CHEMICAL CLEANING COSTS	102
37	FEED ADDITIVE COSTS	104
38	INORGANIC MEMBRANE DEPOSIT ANALYSIS TECHNIQUE	115

TABLES

		PAGE
1	Filtration Test Results	17
2	Coagulation Tests on Activated-Sludge Effluent	19
3	Results of Organic Analysis of Membrane Deposits	27
4	Cleaning Solution Screening Tests	31
5	Effect of Cleaning Agent on Rejection	34
6	Stream Characterization Data - Experiment I	62
7	Reduction of Feed Solutes for Carbon-Treated Secondary Effluent	64
8	Reduction of Feed Solutes for Secondary Effluent	64
9	Stream Characterization Data, October 28, 1970 - Experiment II	73
10	Stream Characterization Data, November 25, 1970	73
11	Chemical Analysis for Primary Effluent	82
12	Reduction of Feed Solutes, Chemically Clarified Primary Effluent	91
13	Stream Characterization Data, January 26, 1971 - Experiment III	93
14	Costs of Cleaning Solutions	99
15	Representative Costs of Municipal Waste Treatment Processes	105
16	Representative Costs of Spiral-Wound Reverse Osmosis Operation	106
17	Estimated Cleaning Costs of Spiral-Wound Reverse Osmosis Operation on Municipal Effluents	107
18	Estimated Total Operating Costs of Several Treatment Combinations	108
19	Physicochemical Treatment Data	122

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The contract was initiated with Gulf Environmental Systems Company. Due to corporate reorganization, the project was last administered by General Atomic Company. The authors of this report are presently with the ROGA Division of Universal Oil Products Company.

SECTION I

CONCLUSIONS

Data obtained during this study have indicated that spiral-wound reverse osmosis units can be operated on primary and activated-sludge effluents with only moderate pretreatment. The principal conclusions drawn from this program are outlined below:

1. Activated-carbon pretreatment was clearly not necessary for successful reverse osmosis unit operation on sand-filtered activated-sludge effluent or chemically clarified, sand-filtered primary effluent.

2. Chemical analysis results showed nearly total removal of turbidity and suspended and colloidal solid material. Dissolved substances were also well rejected. The data indicated that on the average the permeate had:

   a. Less than 7% of the dissolved solids originally present in the feed
   b. No detectable turbidity, color, or suspended solids
   c. Less than 1% of the feed phosphate content
   d. Less than 10% of the feed ammonia nitrogen content
   e. Less than 25% of the feed nitrate content
   f. Less than 7% of the feed chemical oxygen demand (COD) content when operating on secondary effluent
   g. Less than 35% of the feed COD when operating on primary effluent. However, tests indicated that the remaining COD could be lowered to approximately 10% of the feed by aeration.

3. Product water fluxes in the range of 8 to 10 gal./ft^2-day could be maintained by regular chemical cleaning. Three cleaners, the enzyme detergent BIZ, ethylenediaminetetraacetic acid (EDTA), and sodium perborate, performed well in the field tests. Test results indicated that enzymes per se were not useful as cleaners. To prevent membrane damage due to exposure

to high pH, all cleaners were adjusted to a pH range of 7.5 to 8.0. Periodic depressurization also aided in maintaining the product water flux.

4. Experimental results at higher pressures indicated that there was an optimum pressure-membrane permeability combination which would minimize plant cost for a selected output.

5. Salt rejections, determined by conductivity measurements during the activated-sludge effluent tests, remained high throughout the test period and in some cases appeared to increase slightly above the initial value. There was no evidence of membrane degradation in any of the longer-term runs (4900 hr maximum).

6. A simplified economic analysis of cleaning costs indicated that only a small expense is incurred if the interval between cleanings is longer than required for 30 gal./ft^2 to pass through the unit.

7. A rough economic analysis indicated that treatment costs for a combination of primary + secondary + dual media filtration + reverse osmosis and a combination of primary + chemical clarification + dual media filtration + reverse osmosis were comparable (approximately 49¢/1000 gal. at 10 million gallons per day). Brine disposal costs were not included.

8. Comparisons of ion exchange and electrodialysis cost predictions with those estimated for reverse osmosis indicated that above a feedwater salinity of 700 ppm, production of potable water (500 ppm total dissolved solids) by reverse osmosis is more economical. These calculations were based on a membrane life of 3 yr.

SECTION II

RECOMMENDATIONS

Encouraging results obtained from treatment of primary and secondary effluents by spiral-wound reverse osmosis units at Pomona should be supplemented by confirmation tests at other locations and on a larger-size unit to permit accurate prediction of operational economics. Taking into account the effects of water recovery, cleaning of large sections, and operational and maintenance costs, a minimum demonstration plant size of 100,000 gal./day should be considered.

While demonstration of reverse osmosis treatment of sewage effluents on a larger scale is necessary to confirm the economic projections made in this program, additional information on a smaller scale is also needed. This necessary information includes the following:

1. Operation of the reverse osmosis units at higher water recoveries should be attempted in order to determine the maximum possible recovery level. Water recovery at Pomona is presently limited principally by the solubility of calcium sulphate. Essentially two techniques are available to increase the recovery. One involves substitution of HCl for H_2SO_4 addition to the feed and/or the use of threshold inhibitors. The other technique involves the use of brine treatment to remove a significant portion of the organic and sparingly soluble inorganic matter. The supernatant from this step could then be recycled to the reverse osmosis system to greatly increase effective recovery. Ultimately, the amount of recovery possible would be limited by osmotic pressure considerations and permeate quality. However, it is believed that significant gains in recovery are possible with this scheme, which also appears to have potential cost advantages. Removing organics from the brine rather than from the feed would allow smaller vessels, and pumping costs would diminish.

2. The experimental data indicated that there may be an optimum combination of membrane permeability and pressure. These findings should be investigated over a wider range of each parameter to confirm this relationship, which is of great importance in determining the plant size, which in turn influences the capital and membrane replacement costs.

3. Other operating variables, including brine channel turbulence, brine velocity, and brine-to-product flow ratio (recovery), should be studied over a wider range using small modules in parallel treating the same feed stream to find the optimum combination of parameters.

4. Programmed depressurization and prefouling the membrane with an easily removed substance should be investigated more thoroughly. Heated cleaning solutions should also be studied.

5. Membrane replacement is the largest component of the operating cost of a large reverse osmosis plant. Long-term membrane life testing should be continued to determine the effective membrane lifetime when operating on both primary and secondary effluents.

6. Recently developed membranes with high water permeation rates at low pressures but nearly equal salt rejection capability should be investigated to increase the operating water flux and improve economics.

SECTION III

INTRODUCTION

This is the final report on work performed by Gulf Environmental Systems Company under Environmental Protection Agency Contract No. 14-12-831, "Control of Membrane Fouling in Reverse Osmosis Systems Operated on Secondary Effluents," during the period January 27, 1970 to July 27, 1971.

POTENTIAL OF REVERSE OSMOSIS IN TREATING SANITARY WASTES

Any consideration of the future of wastewater treatment and water reutilization must include the use of demineralization processes. Only through these methods will it be possible to approach complete and ultimate wastewater treatment and disposal accompanied by the production of a water for reuse that will meet the most stringent standards. Water that passes even once through a municipal system increases some 250 to 350 mg/l in dissolved solids which include organic and inorganic substances of varied character. Multiple reuse soon compounds the problem unless methods for the reduction of dissolved solids are employed.

The process for water demineralization and concentration of solutes that has recently attracted the greatest attention is reverse osmosis. This is a separation process which is dependent on the semipermeable characteristics of the membrane, that is, on a membrane which will permit some constituents of a solution, generally the solvent, to pass through or permeate it while retaining other components (solutes). Reverse osmosis differs from ultrafiltration and other filtration methods in several ways. The most significant differences are its ability to separate constituents of a solution and the role of the osmotic pressure. Reverse osmosis has the important advantage of organic removal over other demineralization processes such as electrodialysis and ion exchange.

Reverse osmosis is a concentration process and alone does not constitute a complete answer to the problem of ultimate disposal. However, there are certain conditions under which it should receive serious consideration:

1. A reduction in the volume of the wastewater is required or useful.
2. Recovery of valuable or reusable materials is desired.
3. Water conservation or recovery is required or desirable.
4. Efficiency of wastewater treatment is important. With reverse osmosis, it may be possible to achieve this goal by concentrating the undesirable substances in a reduced volume, and thus to reduce the size of some of the major treatment equipment and lower costs.

Among the advantages offered by reverse osmosis are:

1. Its energy requirements are high but not excessive in cost for the quality achieved--6 to 8 Kwh per 1000 gal. of product.
2. It permits operation at ambient temperatures.
3. There is only a small or minor addition of solids to the overall solids budget or mass balance.
4. The process is relatively simple in concept; thus, equipment and operation are uncomplicated.
5. Scale-up of the reverse osmosis modular sections is essentially linear.
6. The product or permeate quality in many respects is superior to the community raw water supply.

Because of the potential advantages of the process, the Environmental Protection Agency has sponsored several pilot studies of reverse osmosis processing of municipal wastewater.

REVIEW OF PREVIOUS WORK

This study is a portion of a three-year pilot plant test program on municipal waste processing by reverse osmosis. The tests have been conducted at the Los Angeles County Sanitation District Pomona Water Renovation Plant, Pomona, California under Environmental Protection Agency sponsorship. The purpose of these tests has been to determine the rejection of important pollutants in the water and the operating characteristics of reverse osmosis on sanitary wastewater.

The initial pilot plant tests at Pomona were conducted under EPA Contract No. 14-12-181 on two nominal 10,000 gal./day ROGA reverse osmosis systems.(1) Results showed that spiral-wound modules employing modified cellulose acetate membrane rejected inorganic salts and chemical oxygen demand (COD) of activated-sludge and carbon-treated activated-sludge effluents very well. The early tests identified membrane fouling as the most important operational problem, and most of the effort since that time has been directed toward developing methods of fouling prevention and control.

Mechanical and chemical cleaning methods were investigated for operation on activated-sludge and carbon-treated activated-sludge effluents. It was discovered that BIZ enzyme detergent could be used intermittently to restore the permeate flux. However, its optimum pH was 10, which was in the region of high membrane deterioration rate. Mechanical cleaning methods, such as air-water flushing, were only partially successful in maintaining product water flux.

A closely related investigation of membrane fouling prevention and control was performed by Gulf Environmental Systems under Office of Saline Water

Contract No. 14-01-001-2225.(2) The purpose of that study was to systematically study the membrane fouling characteristics of sewage-contaminated surface waters and to develop techniques for prevention and/or cleaning. Laboratory experiments were conducted to characterize sewage-contaminated surface waters and to evaluate various feed additives. Field tests at the Santee Water Reclamation Facility near San Diego were run with a small reverse osmosis unit to determine the effects of operating variables, such as brine velocity, pressure, brine-to-product flow ratio, and brine-channel turbulence. Samples of membrane from these tests were used for laboratory evaluation of chemical cleaners. Other fouled membranes were cleaned in the laboratory using the most promising techniques derived from the membrane sample tests.

Chemical analyses indicated that fouling deposits on the membrane surface were composed principally of clay, silica, organic acids, polysaccharides, and small amounts of calcium. The organic acid fraction predominated; it was comprised principally of material that contained aromatic hydroxyl groups similar to humic or fulvic acid. Calcium appeared to be cross-linking the organic compounds into less mobile three-dimensional structures. Scanning electron microscope photographs indicated amorphous noncellular material, which was in accord with the chemical analysis.

Fouling-rate test results indicated that membrane permeability and pressure were the most significant variables. Experimental data suggested that an optimum pressure exists for a given feedwater and cleaning frequency based on the quantity of product water produced in a given time.

Cleaning studies indicated that sodium perborate, BIZ enzyme detergent, and ethylenediaminetetraacetic acid (EDTA) performed equally well in restoring the membrane water production capability. All cleaners were adjusted to a pH range of 7.5 to 8.0 in order to prevent membrane deterioration.

Under Office of Saline Water sponsorship, Oak Ridge National Laboratory has studied the effects of hydrodynamics upon tubular reverse osmosis system performance. A portion of that study was an investigation of the effects of brine velocity upon membrane surface fouling. Shepphard and Thomas(3) have reported data covering a velocity range of 0.09 to 24 ft/sec with a pressure range of 200 to 1200 psig. The feed was either demineralized water or river water spiked with $MgCl_2$ to give solution concentrations of 0.04M to 0.08M.

When using the demineralized water feed (0.044M $MgCl_2$), the ORNL workers observed essentially no flux decline at 800 psig and an axial velocity of 24 ft/sec over a 93-hr run. This was a very surprising result in view of the large amount of published data which show a marked flux decline in the first few hours of operation, usually attributed to membrane compaction. The ORNL workers believed that the high circulation velocity was the principal factor contributing to water flux maintenance.

In a similar run with untreated Tennessee River water (10 to 100 ppm suspended solids) at 800 psig, only a moderate decline (from 28 to 23.5 gal./ft^2-day) was observed during a 66-hr run at 24 ft/sec axial velocity. When the velocity was reduced to 1.64 ft/sec, the flux dropped off quickly to 10 gal./ft^2-day. Shepphard and Thomas did not chemically analyze the membrane deposit. They stated that it was a yellow-brown solid that was easily removed with a jet from a laboratory wash bottle and a soft camel-hair brush. All experiments were performed in a closed-loop fashion.

An earlier Oak Ridge study(4) was concerned with the use of dynamic membranes formed from polyelectrolytes or fine-grained supports for reverse osmosis processing of primary and secondary effluent. Some cation exchange membranes exhibited salt rejections of 50% at permeate fluxes higher than 50 gal./ft^2-day. However, very high circulation velocities (greater than 20 ft/sec) were required to maintain the flux and rejection.

Smith, Masse, and Miele(5) summarized tests conducted at Pomona, California and Lebanon, Ohio on tubular and spiral-wound units. Results at both locations indicated that BIZ enzyme detergent had superior cleaning ability compared with several other cleaning formulations. The role of reverse osmosis in advanced waste treatment was analyzed by comparing stepwise replacement of tertiary and secondary treatment by reverse osmosis. It was concluded that more favorable costs were obtained when reverse osmosis was used near the primary treatment end of the wastewater processing sequence.

An extensive comparison of operating characteristics of several reverse osmosis unit designs was conducted under EPA sponsorship at Hemet, California. Feeds to the reverse osmosis units included chlorinated secondary effluent with varying degrees of tertiary treatment, including sand filtration, diatomaceous earth filtration, alum coagulation, and activated carbon. A final report of the study is being printed.(6)

PURPOSE AND SCOPE

The purpose of the work performed under this contract has been to obtain reverse osmosis operating data for primary and secondary effluents with varying degrees of pretreatment. Five different reverse osmosis feed streams have been investigated: primary effluent with and without sand filtration, sand-filtered activated-sludge effluent, chemically clarified primary effluent with sand filtration, chemically clarified primary effluent with sand filtration and carbon pretreatment, and activated-carbon-treated secondary effluent. The nominal 10,000-gpd units used in the previous study have been modified to incorporate provisions for chemical and mechanical cleaning. Figure 1 is a schematic diagram of the feed streams.

An experimental and cleaning unit was also constructed. It contains pretreatment provisions plus two parallel reverse osmosis systems. One system consists of a 10-ft standard pressure vessel that will accommodate three production spiral-wound modules. The other system, for studying the effect of several levels of operating parameters at the same time on the same feed, can accommodate up to twelve 5-ft^2 modules in parallel.

Four major field experiments were conducted. In the first, a comparison of operation on activated-sludge effluent with and without activated-carbon pretreatment was made. The purpose of the second experiment was to compare

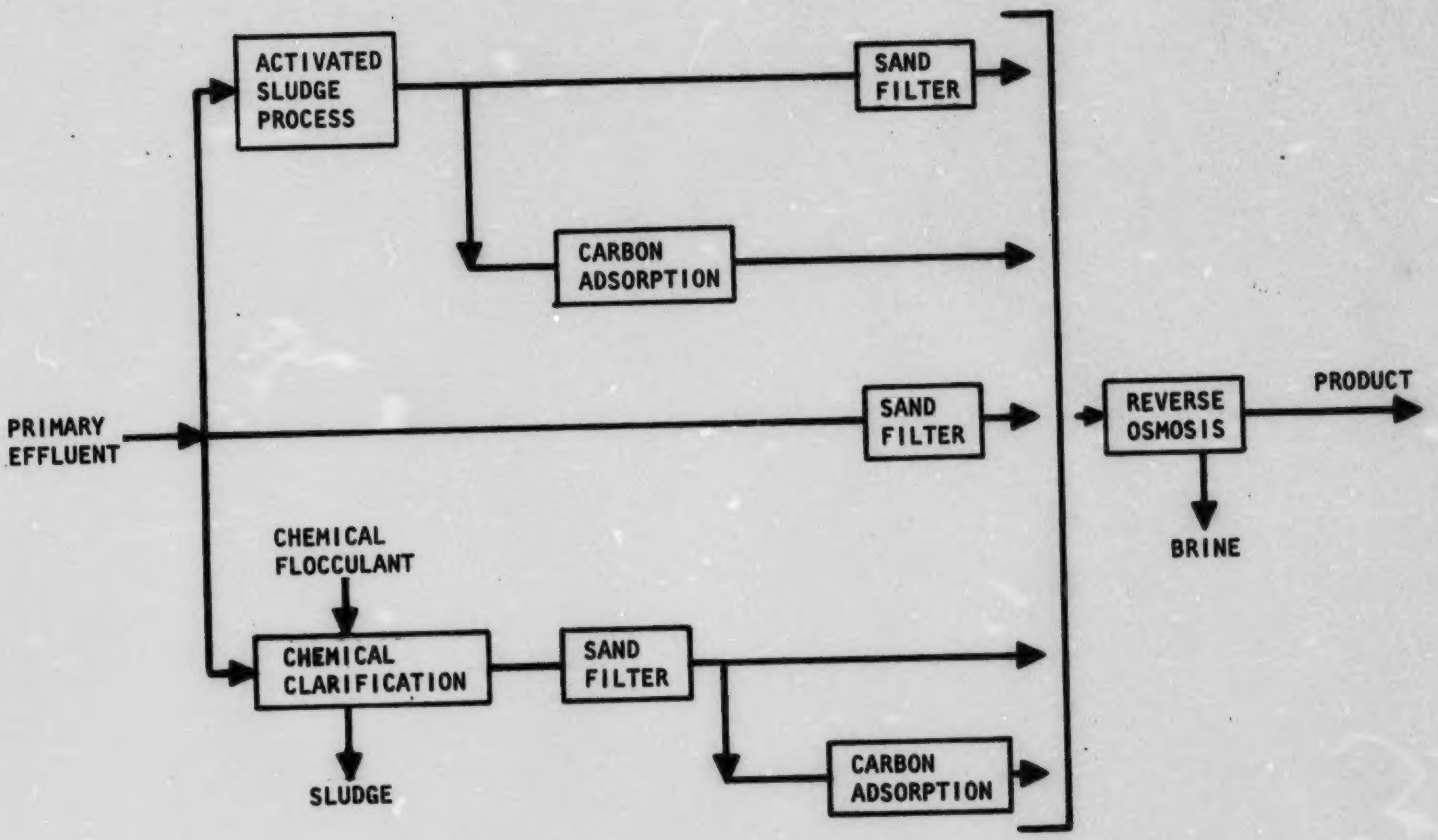

ACTIVATED SLUDGE PROCESS
SAND FILTER
CARBON ADSORPTION
PRIMARY EFFLUENT
SAND FILTER
REVERSE OSMOSIS
PRODUCT
BRINE
CHEMICAL FLOCCULANT
CHEMICAL CLARIFICATION
SLUDGE
SAND FILTER
CARBON ADSORPTION

Fig. 1. Reverse osmosis unit feed streams

different chemical cleaning techniques with activated-sludge effluent. In the third experiment, the reverse osmosis units were operated on chemically clarified primary effluent with and without activated-carbon pretreatment. Finally, in the fourth experiment, actual plant operation was more closely simulated by running a reverse osmosis unit on activated-sludge effluent at constant product flow.

SECTION IV

CLEANING AND PRETREATMENT TECHNIQUE DEVELOPMENT

Water flux maintenance techniques were approached in two ways: pretreatment to prevent or minimize membrane fouling and cleaning to remove fouling layers. A number of feed characterization techniques were evaluated to predict the fouling tendency of feed streams and to aid in selecting pretreatment methods. Membrane deposits were chemically analyzed to determine which compounds in the feed became attached to the membrane surface. Cleaning techniques were first screened on small fouled membrane samples and then tested on fouled modules. Mechanical removal techniques, such as air-water flow, were evaluated. The effect of small chlorine additions to the feed upon membrane lifetime was determined.

FEEDWATER CHARACTERIZATION TECHNIQUES

Several feed characterization methods were examined to predict the fouling tendency of a feed stream and to aid in the development of pretreatment techniques. The following tests were used:

1. Conventional mineral analysis, pH, COD, and turbidity
2. Silting index
3. Ultraviolet absorbance at 275 mμ and total organic carbon (TOC)
4. Hydroxylated aromatic material as "humic acid"
5. Electrophoretic mobility or streaming current

The tests in item 1 were performed regularly by Los Angeles County Sanitation District personnel. These are standard wastewater tests. The tests in items 2, 3, 4, and 5 were performed by Gulf Environmental Systems to gain more insight into the fouling tendency of the feedwater.

To correlate feed properties with membrane fouling, a gross test, suitable for field operation, was required to supplement the particle size analysis. A simple experiment showed that the nephelometric turbidity test has little value in characterizing or predicting fouling. By using a water sample that was prepared by diluting water containing a slime removed from a badly fouled module, the following data were obtained:

Sample	Turbidity (JTU)	Filtration Time[a] (sec)
Distilled water	0.10	40
Dilution of slime in distilled water	0.35	620
Laboratory tap water	0.93	80

---

[a] 250-ml sample, 0.45-μ membrane.

No correlation between turbidity and fouling was observed.

The silting index technique(7) is based on the measurement of filtration time for three consecutive volumes through a selected area of filtration and membrane filter of specified porosity under constant pressure. The silting index is thus a dimensionless number that is directly related to the amount of ultrafine particles in the fluid:

$$SI = \frac{T_3 - 2T_2}{T_1} ,$$

where SI = silting index,

T_1 = filtration time for V_1,
T_2 = filtration time for V_2,
T_3 = filtration time for V_3,
$V_3 = 2\ V_2 = 10\ V_1$.

This technique is suitable for field operation and appears to be more sensitive to variations in both organic and inorganic particulate matter than nephelometric turbidity. A 0.45-μ Millipore membrane filter was used for the tests.

Organic matter was measured with the Beckman TOC analyzer and UV spectrophotometer. The TOC measurements were made on filtered and unfiltered samples but lacked precision at low concentrations. Ultraviolet absorbance at 275 mμ appears to offer promise as a precise field technique. Dobbs, et al.,(8) have reported a linear relationship between the TOC in polluted streams and UV absorbance in the wavelength range from 250 to 300 mμ. Data in Reference 2 have confirmed this linear relation on sewage-contaminated waters. Because turbidity itself contributes to the UV absorbance reading, samples were filtered through No. 42 Whatman paper. Thus, the correlation between UV absorbance and turbidity should be valid only for waters having a similar amount of particulate organic matter. Oxidation state also appears to be a variable.(2)

There is considerable experimental evidence that colloids of the humic acid type are an important factor in municipal wastewaters. Rebhun and Manlea(9) reported that 40% to 50% of the TOC of trickling filter secondary effluent consisted of humic substances (humic, fulvic, and hymatomelanic acids). The remaining organic matter consisted of ether-extractables, 8.3%; anionic detergents, 13.9%; carbohydrates, 11.5%; proteins, 22.4%; and tannins, 1.7%. Kononova(10) had previously reported that about 20% of the manure applied to the soil is fixed in the form of humus, the rest being mineralized. Abrams(11) and Rebhun and Kaufman(12) found that sorption behavior of the bulk of municipal effluent organics was similar to that of humic compounds. Another parallel between humic acids of biological treatment plant effluent and natural origin with respect to the behavior in chemical flocculation and filtration processes was drawn by Rebhun, et al.(13)

Humic acid can be destabilized by the addition of acid.(10) Hence, there may be a direct correlation between the amount of this type of material in the feedwater and membrane fouling. Humic acid represents a class of compounds of unknown structure, which makes quantitative determination impossible. In the present work, hydroxylated aromatic material was measured colorimetrically using the phosphomolybdic acid method(14) and humic acid standards. The color intensity measured with this method depends upon the number and location of hydroxyl groups, rather than the total number of moles of a particular chemical compound. Thus, exact correlation of samples and standards and comparison with the TOC cannot be obtained.

The fifth characterization technique employed was a measurement of the electrokinetic properties of the feedwater colloids. After investigating several electrokinetic measurements, such as electrophoresis and zeta potential, streaming current was selected as the best method for field measurement. The device employed, a Hydroscan (Leeds and Northrup), did not measure the true streaming current of the colloid-membrane system. Instead, it measured the electric effects associated with a Teflon plug-metal ring system. It was useful in measuring isoelectric points; however, these streaming current measurements could not be correlated with any electric phenomenon associated with reverse osmosis operation.

The process streams were measured by these techniques periodically throughout the test program to determine the effectiveness of the various pretreatment steps. Test results are presented in Section V.

PRETREATMENT EXPERIMENTS

Laboratory experiments were conducted to determine the effects of acid addition and calcium ion concentrations upon the fouling characteristics of the secondary effluent feed. Some exploratory tests were also performed to establish the feasibility of further clarification of the activated-sludge effluent using chemical coagulants.

Laboratory experiments on raw feed showed that the turbidity passed through a maximum at a pH of 1.5 to 2.4. To determine what size particle was being affected by this acid addition, samples were acidified and filtered through 0.22-μ, 0.45-μ, and 0.8-μ Millipore membrane filters. The results showed a decrease in the fraction below 0.8 μ and an increase in the fraction above 0.8 μ as compared with unacidified controls. This indicated that an increase in particle size occurred as the result of acid addition.

Effects on water recovery of pretreatment (acid addition) and calcium ion concentration increase were investigated by 0.45 μ membrane filter plugging tests. It was suspected that turbidity increases in the secondary effluent as it passed through the unit could be caused by a lowering of pH and an increase of calcium ion concentration. Turbidity increases would decrease membrane filtration rate.

A fixed feed volume of 500 ml was used for each test. Change in membrane permeability caused by passage of the fixed feed volume was determined by comparing the distilled water filtration rate before and after feed volume passage.

After each fixed feed volume test, each membrane filter was soaked in 200 ml of distilled water for 15 minutes. Then the flow rate was again measured with a fixed volume of distilled water. Little change occurred as a result of soaking. Table 1 shows the test results.

Table 1
FILTRATION TEST RESULTS

	Fixed Feed Volume Test		Soak Test	
			Filtration Rate (ml/min)	
	Percent Permeability Based on Raw Feed	Percent Equivalent Recovery on Pomona Feed	Before Soaking	After Soaking
Raw feed, pH ∿7.5	100		32	30
Raw feed, pH 3.4	23		7.1	6.8
Raw feed, pH 4.2	40		9.8	12.1
Raw feed + 0.2 g $CaCl_2$	67	52	19	20
Raw feed + 0.5 g $CaCl_2$	53	73	14	16

The filtration test results show that acid addition and an increase in calcium ion concentration can greatly lower the raw feed filtration rate. Because of these effects, a feed tank, which provided about 15 minutes of residence time for particle growth, and the sand filter were placed downstream of the acid addition point. Even with those precautions, the treated feed often had higher turbidity levels than the raw feed.

Secondary effluent obtained at Pomona on June 5, 1970 was subjected to a series of coagulation and settling tests. The purpose of these experiments was to determine in a preliminary fashion the feasibility of further clarification of secondary effluent using common flocculants.

Coagulation tests were run with a streaming current detector (Leeds and Northrup Hydroscan) and with a multiple stirrer. The polyelectrolyte Magnifloc 521C (American Cyanamid) was chosen for these tests because it had already proved effective and is approved by the Food and Drug Administration for potable water. The colloidal matter in the samples was negatively charged. Iron was used as the inorganic flocculant rather than aluminum because the hydroxide is more insoluble at lower pHs. The results (see Table 2) show the turbidity of the untreated secondary effluent to be due mainly to particles of <8 μ. After coagulation, the overall turbidity increases, but the turbidity in the <8-μ fraction and especially in the <0.45-μ fraction decreases. This indicates that agglomeration is occurring. Whether this agglomeration would actually improve the quality of a reverse osmosis unit feed depends entirely on the efficiency of the sand filter. The settling time was found to be too long to be practical.

After filtration, the membrane filters were examined and found to contain little morphological material. The filter from the pH 3.5 test was darker than that from the untreated feed test, which was almost white. The filter from the Magnifloc 521C test was brown, which indicated clay. X-ray fluorescence tests also showed much more iron in the filter with only Magnifloc 521C. This indicated agglomeration of clay when the Magnifloc 521C was used alone. However, lower turbidities were obtained using both $FeCl_3$ and Magnifloc 521C.

These results indicate that coagulation with these agents would be beneficial if clay were a significant membrane fouling material. However, since the membrane deposits were principally organic, this approach was not pursued further. Evidently, while clay is present in the secondary effluent, it does not significantly foul the membrane but remains in the concentrate.

TABLE 2
COAGULATION TESTS ON ACTIVATED-SLUDGE EFFLUENT

Group I - Hydroscan with Stirring

Sample	pH	Coagulant Type	Coagulant Dosage (ppm)	Streaming Current (µA)	Elapsed Time	Turbidity (JTU)				UV Absorbance at 275 mµ after Filtration through No. 42 Paper
							After Filtering			
						Super-natant	No. 42 Paper	<8-µ Fraction	<0.45-µ Fraction	
6/5-70	7.55			-30	0	1.1				0.148
					15 hr	0.9	0.9			
6/5-70	3.50			-18	0	1.8				
					1/2 hr	1.8				
					15 hr	1.1	0.8			
6/5-70	3.50	Magnifloc 521C	1.9	+0.2	0	4.5				
					15 hr	4.4	1.6			0.120
6/5-70		FeCl$_3$ +	50	+15	0					
		Magnifloc	5.6	+0.8	0	12				
		860A			15 hr	3.3	0.36			0.109

Group II - Multiple Stirring Apparatus

Sample	pH	Coagulant Type	Coagulant Dosage (ppm)	Streaming Current (µA)	Elapsed Time	Turbidity (JTU)				UV Absorbance at 275 mµ after Filtration through No. 42 Paper
							After Filtering			
						Super-natant	No. 42 Paper	<8-µ Fraction	<0.45-µ Fraction	
6/12-70	7.1				0	0.8				0.138
					10 min	0.9				0.131
				-25	16 hr	0.9		0.77	0.38	0.130
6/12-70	3.5				0	0.9				
					10 min	1.2				
				-16	16 hr	1.3		0.59	0.21	0.132
6/12-70	3.5	Magnifloc 521C	1.9		0	0.9				0.132
					10 min	3.7				0.123
					16 hr	3.9		0.47	0.25	0.128
		FeCl$_3$ +	50		0	0.9				0.131
		Magnifloc	5.6		10 min	2.7				0.123
		860A			16 hr	2.9		0.29	0.17	0.102

TABLE 2 (Continued)
Group III - Multiple Stirring Apparatus

Sample	pH	Coagulant Type	Coagulant Dosage (ppm)	Streaming Current (μA)	Elapsed Time	Turbidity (JTU)			
							After Filtering		
						Super-natant	No. 42 Paper	<8-μ Fraction	<0.45-μ Fraction
6/12-70	7.1				1-1/2 hr	0.78			
					16 hr	0.75		0.63	0.50
6/12-70	3.5				1-1/2 hr	1.0			
					16 hr	0.98		0.53	0.25
6/12-70	3.5	Magnifloc 521C	1.7		1-1/2 hr	2.5			
				-20	16 hr	2.4		0.66	0.21
6/12-70	3.5	$FeCl_3$ +	50		1-1/2 hr	2.0			
		Magnifloc 521C	0.8	-16	16 hr	1.6		0.38	0.19

Group III - Multiple Stirring Apparatus, After 16 Hr

Sample	pH	Coagulant Type	UV Absorbance at 275 mμ After Filtration		Total Organic Carbon (ppm)		Fe on 8-μ Millipore Filter
			No. 42 Paper	0.45-μ Fraction	Unfiltered	0.45-μ Fraction	
6/12-70	7.1			0.129	11	8	70
6/12-70	3.5			0.117	11	8	60
6/12-70	3.5	Magnifloc 521C		0.107	10	8	170
6/12-70	3.5	$FeCl_3$ + Magnifloc 521C		0.098	11	8	

ANALYSIS OF MEMBRANE DEPOSITS

The objective of the membrane deposit analyses was to determine which compounds in the feed became attached to the membrane surface. These results greatly aided in the search for effective chemical cleaning formulations.

Method

Inorganic and organic analyses were carried out on the membrane deposits. The inorganic analysis samples were dried at 105°C, and the organic analysis was performed on material as removed from the membrane surface. A detailed description of the inorganic analysis scheme is presented in Appendix A. It includes an extraction with dilute hydrochloric acid and determination of iron, aluminum, calcium, magnesium, and sulfate in the extract. Clay minerals were not dissolved by this extraction and thus were left in the residue. Clay and total silica in the residue were determined using hydrofluoric acid. The advantage of this scheme is that iron deposited as iron phosphate is determined separately from iron deposited in clay. Semiquantitative spectrographic analyses were also obtained.

Organics, roughly determined by the loss on ignition at 600°C, were then successively extracted with various reagents. An aqueous extraction gave the fraction soluble or dispersible in water. This was followed by a 5% sodium bicarbonate extraction which yielded a fraction consisting of carboxylic and sulfonic acids. Finally, 5% sodium hydroxide extraction fractions included not only phenolic compounds but also products resulting from saponification. Hexane-soluble material was determined according to Ref. 14. This fraction included nonvolatile fats, waxes, oils, and other esters, acids, and ketones. Kjeldahl nitrogen analyses for organically bound nitrogen were also carried out.(14) Total organic carbon, UV absorbance for aromatics, and hydroxyaromatic tests were determined on each fraction. Infrared analyses were made by either pressing the dry sample into a potassium bromide pellet or filtering a solution through TH paper, a very thin transparent membrane filter supplied in matched pairs.

Results

Analyses were performed on membrane deposits resulting from operation on both primary and secondary effluents. Inorganic analyses of membrane deposits obtained during secondary effluent operation throughout the contract were very similar.

Before field operations began, a deposit from Phase V extensions with secondary effluent feed was analyzed to determine the inorganic content. The results were as follows:

	Percent of Total
Loss on ignition at 600°C	73.3
Silica (total including clay)	14.0
Carbonate	<1.0
Residue (after silica removal)	8.6
Iron (non-clay)	<0.3
Aluminum (non-clay)	<0.3
Calcium (non-clay)	1.7
Magnesium (non-clay)	<0.5
Sulfate	<2.0

The high loss of weight on ignition is evidence that the deposit was principally organic. Examination of the deposit under magnification indicated live aerobic microorganisms, principally bacteria.

Additional membrane deposits from secondary effluent operation in Experiments I and IV were analyzed. Membranes operated on carbon-treated secondary effluent did not contain enough deposits for analysis. The deposits on one of the lead modules and one of the end modules, which were operated on sand-filtered secondary effluent in Experiment I, had the following composition:

	Percent of Total	
	Lead Module	End Module
Loss of weight on ignition at 600°C	58.0	69.1
Kjeldahl nitrogen	3.0	3.8
Hexane-soluble material	2.8	2.3
CO_3	<2.0	<2.0
Residue (silica, clay, etc.)	35.0	24.5
Iron (non-clay)	<0.3	<0.3
Aluminum (non-clay)	<0.3	<0.3
Calcium (non-clay)	1.1	1.9
Magnesium (non-clay)	<0.5	<0.5
SO_4	<2.0	

These results indicate a rather uniform deposit. There appeared to be a tendency for more clay to be deposited in the lead modules and more organics toward the end modules.

Emission spectrographic analysis showed only the silicon content was greater than 1%. The hexane-soluble fractions were tested for fatty acids between C_{10} and C_{22}, but negative results were obtained. Technical-grade humic acid was also analyzed. Hexane-soluble material was 4.7% and Kjeldahl nitrogen was 0.43%.

Over one year later a module was removed from Experiment IV and analyzed. The following results were obtained on the dried deposit:

	Percent of Total
Loss of weight on ignition at 600°C	69.4
CO_3	<0.5
SiO_2	13.1
Residue (non-silicate portion of clay; certain acid-insoluble compounds)	9.5

	Percent of Total
Iron (non-clay)	0.4
Aluminum (non-clay)	<0.03
Calcium	0.8
Zinc	<1.0
Copper	2.4

After the acid extraction for the inorganic analysis, the sample was extracted with 5% NaOH. A neutralized portion of this basic extract showed an UV absorbance 10 times as high as the acid extract. This indicated an acidic nature of the aromatic material. Unfortunately, it was not possible to precipitate this material and obtain a weight because on acidification it formed a colloidal dispersion. The residue was found to contain iron but no copper.

The spectographic results in all cases showed no deposit from the cleaners, i.e., no borate or phosphate compounds. The deposit was principally acidic aromatic organic material with some silicates.

Membrane deposits were analyzed from the primary effluent tests with three pretreatment levels: sand filtration, chemical coagulation plus sand filtration, and chemical coagulation plus activated-carbon treatment. The membrane deposit obtained from operation on sand-filtered primary effluent was very high in organic matter:

	Percent of Total
Loss of weight on ignition at 600°C	76.0
Kjeldahl nitrogen	0.9
Hexane-soluble material	23.0

Membrane deposits removed early in Experiment III from the units operating on chemically clarified primary effluent with and without additional carbon treatment indicated carryover of iron compounds from the clarifier.

The following analysis was obtained with carbon-treated effluent:

	Percent of Total
Loss of weight on ignition at 600°C	40.6
Carbonate	<0.5
Silica	0.4
Residue (insoluble material such as non-silicate portion of clay)	1.0
Calcium (non-clay)	<0.5
Aluminum (non-clay)	<0.3
Magnesium (non-clay)	<0.5
Sulfate (non-clay)	<2.0
Iron	24.3

The dried material was yellow and powdery. After ignition a black residue was obtained. Optical emission analysis of the dried deposit showed only iron and phosphorous contents >1%, and x-ray fluorescence also indicated iron phosphate. The material was amorphous, so x-ray diffraction measurements could not be made.

Additional modules were removed a month later from Unit I, running on carbon-treated clarified primary effluent, and Unit II, running on sand-filtered clarified primary effluent, and the dried deposits were analyzed. This time the deposits were both black and the ignited residues were reddish-brown. The module from Unit I did not have much material in it; the module from Unit II was more heavily fouled. Results obtained on Unit I material and Unit II material were as follows:

	Percent of Total	
	Unit I	Unit II
Loss of weight on ignition at 600°C	36.1	56.1
Total Kjeldahl nitrogen	2.4	2.4
Hexane-soluble material	3.3	14.1
Iron (spectrographic)	>1.0	>1.0
	>1.0	>1.0

Results indicated that activated carbon was effective in removing hexane-soluble compounds but not nitrogen compounds. The deposit from Unit II gave a positive ninhydrin reaction, specific for proteins and amino acids. Again, the deposit on Unit I was mostly iron phosphate. The deposit on Unit II contained about 65% iron phosphate, the balance being mostly organics. Because of these results, EDTA was employed as a cleaner in both units instead of sodium perborate. A noticeable increase in permeate flux resulted.

Organic analyses were made on the deposit from the lead module in Experiment I (secondary effluent) and on the deposit from the test using sand-filtered primary effluent. During extraction, the mixtures were stirred for 1 hr and centrifuged. Results are listed in Table 3. The designation "A" refers to hydroxylated aromatic material calculated as mg/l humic acid. The designation "B" is equal to $A/_{UVX100}$ and is a rough measure of the extent of hydroxylation of the total amount of aromatic material.

All extracts gave positive Moslisch's tests for carbohydrates, especially the NaOH fractions. All gave negative Biuret tests for peptide linkages except primary NaOH I. Suspensions of the solid deposits were given the Biuret test: the secondary effluent deposit was negative, and the primary effluent deposit was positive. However, the primary deposit gave a negative ninhydrin test for proteins. Suspensions of the unextracted samples were treated with 10 drops of HCl and allowed to stand overnight. Positive Fehling's tests were then obtained on both samples. Using the Folun-Wu method,(15) the secondary effluent deposit was found to contain 0.6% starch measured as glucose and the primary deposit to contain 0.2%. The NaOH extracts, which showed a lower proportion of aromatics, were analyzed for fatty acids between C_{10} and C_{22} with negative results.

TABLE 3

RESULTS OF ORGANIC ANALYSIS OF MEMBRANE DEPOSITS

Extract Fraction	TOC (mg/1)	UV Absorb at 275 mμ	$\frac{UV \times 10^3}{TOC}$	Percent Total TOC Extracted	A	B	Fehling's Test	Iodine Test for Starch
			Secondary Effluent Deposit					
Aqueous I	825	5.00	6.1		335	0.7	Neg.	Neg.
Aqueous II	340	1.56	4.6					
Aqueous III	229	1.24	5.4					
Aqueous IV	142	0.737	5.2	48.8				
5% $NaHCO_3$ I	209	1.62	7.8		80	0.5	Neg.	Neg.
5% $NaHCO_3$ II	168	1.17	7.0					
5% $NaHCO_3$ III	90	0.723	8.0					
5% $NaHCO_3$ IV	81	0.542	6.7	17.4				
5% NaOH I	950	2.33	2.5		423	1.8	Neg.	Pos.
5% NaOH II	85							
5% NaOH III	28			33.8				
			Primary Effluent Deposit					
Aqueous I	238	1.39	5.8		135	1.0	Neg.	Neg.
Aqueous II	131	0.820	6.3					
Aqueous III	128	0.376	2.9					
Aqueous IV	157	0.308	2.0	18.8				
5% $NaHCO_3$ I	888	3.58	4.0		398	1.1	Neg.	Neg.
5% $NaHCO_3$ II	569	1.52	2.7					
5% $NaHCO_3$ III	263	0.790	3.0					
5% $NaHCO_3$ IV	158	0.531	3.4	53.9				
5% NaOH I	823	2.94	3.6		505	1.7	Neg.	Pos.
5% NaOH II	98							
5% NaOH III	29			27.3				

Infrared analysis of these samples indicated the following compounds as the most likely to be present:

Secondary Effluent Deposit

Aqueous extract: carboxylic acids, ethers, alcohols and phenols
5% $NaHCO_3$ extract: carboxylic acids, ethers, esters and ketones, alcohols and phenols
5% NaOH extract: carboxylic acids, aromatic ethers, esters and ketones, alcohols and phenols, 1:2, 1:2:3, and 1:4 substituted aromatics
Hexane extract: ketones, phenols and alcohols, 1:4 disubstituted aromatics

Primary Effluent Deposit

Aqueous extract: gypsum
5% $NaHCO_3$ extract: carboxylic acids, aromatic ethers, esters, 1:4 disubstituted atomatics
5% NaOH extract, insoluble in basic solution: carbonate, carboxylates, alcohols and phenols
5% NaOH extract acidified: carboxylic acids, phenols and alcohols, ethers
Hexane extract: carboxylic acids, esters and ketones, aliphatic ethers

The primary membrane deposit was again analyzed for hexane-soluble material, hydrocarbons, fatty matter, and methylene blue active substances. Results were as follows:

	Percent of Total
Hexane-soluble material	30.0
Hydrocarbons	1.4
Fatty matter	29.0
MBAS	0.39

Reference 14 describes "fatty matter" as being polar material which will absorb on alumina such as fatty acids and esters. MBAS includes not only alkylbenzene sulfonates but also alkyl sulfates.

The conclusions drawn from the organic membrane deposit analyses were:

1. Starches, hexoses, aldehydes, proteins, amino acids, C_{10}-C_{22} fatty acids and fats, hydrocarbons, detergents, and soaps all play a very minor role, if any, in the membrane deposits.

2. The membrane deposits do contain large amounts of polyhydroxy aromatic matter which also contains carboxylic acid groups.

3. Inorganic matter is present usually in small amounts. However, it may still be important in establishing cross-linked, three-dimensional structures with the organic acids.

4. Ferric salts, probably resulting from clarifier carryover, comprised a large fraction of the membrane deposits when chemically clarified primary effluent was used.

CLEANING TECHNIQUE SCREENING

Chemicals for cleaning fouled membrane were first screened by exposing small samples and measuring the water permeation rate before and after the treatment. The membrane samples were taken from modules operated approximately 5000 hr on activated-sludge effluent during Phase V of Contract No. 14-12-181. Samples of membrane cut from modules were placed in a pressure cell apparatus. The test conditions were as follows:

Membrane area	40 mm^2
Backing material.	D-601 sailcloth as attached to membrane cut from the module
Operating test pressure	400 psi
Test solution	Distilled water

Fouled membrane samples were placed in the test unit, and a 10-min flow reading was taken. The samples were subjected to a cleaning treatment, and another 10-min flow reading was then taken. This approach yields some measure of the relative effectiveness of various cleaning methods through observation of the percentage difference of flow rates before and after treatment. These test results are not immediately transferable to modules because the hydrodynamic factors are not present. The pressure cell apparatus is not capable of accurately measuring salt rejection because of the stagnant conditions in the cell. Membrane deterioration tests were conducted on standard membrane test cells with 10,000 ppm NaCl.

In the preliminary tests six samples were run at one time. One cleaning treatment was used for two samples, and a second method was used for another two samples; the remaining two samples were soaked in distilled H_2O as a control. Membrane samples that were ultrasonically cleaned for 10 min were used as a reference as to complete cleanliness. As the test program progressed, the capability was increased to eight samples.

Results of the screening tests are presented in Table 4. These results indicated that heated urea and sodium perborate were good cleaning agents for this particular deposit. The enzyme detergent BIZ did not significantly increase the water flux. Perhaps this was because the deposit was composed of matter that had survived the numerous BIZ cleanings during the test period.

The heated urea treatments gave very good results. Urea is an excellent hydrogen bond breaking agent. It is a weak base ($K_B = 1.5 \times 10^{-14}$ at 25°C) and appears to be effective at low and high pH. The primary disadvantage of urea is that strong concentrations (6M) and heated solutions were necessary to attain good membrane cleaning in the laboratory. The addition of sodium bicarbonate and boric acid to the cleaning solution was initiated in order to provide pH adjustment to prevent possible membrane attack. Also, it was hoped that the bicarbonate would aid in neutralizing any organic acids that might be present in the deposit. Finally, it was thought that the boric acid might possibly aid in complexing other deposit materials. Whether any of these situations actually occurred is unknown. However, it appears that the bicarbonate addition

TABLE 4
CLEANING SOLUTION SCREENING TESTS

Treatment	Water Flux Difference After Treatment (%)
Urea 6M, pH 5, 60 min, 22°C	+12
Pluronic detergent L61, 1.5%, pH 7.2, 60 min, 22°C	-5
Deriphat detergent 154, 1.5%, pH 11.8, 60 min, 22°C	-8
H_2O, 60 min, 22°C	+1
Urea 6M, pH 5, 60 min, 22°C	+10
BIZ, 1.5%, pH 10, 60 min, 22°C	+2
Sodium perborate, 1.5%, pH 9.8, 60 min, 22°C	+11
H_2O, 60 min, 22°C	+6
Urea 6M, pH 5, 60 min, 22°C	+13
BIZ, 1.5%, pH 10, 60 min, 22°C	+2
Sodium perborate, 1.5%, pH 9.8, 60 min, 22°C	+17
H_2O, 60 min, 22°C	+8
BIZ, 1.5%, 60 min, 22°C	+4
Tripolyphosphate, 1.5%, pH 9.2, 60 min, 22°C	+9
Ammonium bifluoride, 1.5%, pH 3.5, 60 min, 22°C	+5
H_2O, 60 min, 22°C	+5
Urea 4M, pH 5.5, 60 min, 45°C	+22
Urea 6M, pH 5, 60 min, 45°C	+33
Urea 8M, pH 4.8, 60 min, 45°C	+30
H_2O, 60 min, 45°C	+8
Urea 6M, pH 5, 30 min, 45°C	+23
Sodium perborate, 1.5%, pH 9.8, 60 min, 45°C	0
BIZ, 1.5%, pH 10, 30 min, 45°C	+1
H_2O, 30 min, 45°C	+12
Urea 6M, pH 5, 60 min, 45°C	+30
Acetic acid, 4%, pH 2.3, 60 min, 45°C	+5
H_2O, 60 min, 45°C	+5
BIZ, 1.5%, pH 10, 30 min, 22°C	+4
H_2O, 30 min, 22°C	+3
Ultrasonic clean, 10 min	+23
1.5% sodium perborate + 1.5% boric acid, pH 7.9, 50°C, 30 min	+20
Urea 6M, pH 6.5 (HCl), 50°C, 30 min	+14
H_2O_2, 2%, pH 4.8, 50°C, 30 min	+9
H_2O, pH 6.8, 50°C, 30 min	0
H_2O, 2%, + $NaHCO_3$, pH 7.5, 50°C, 30 min	+1
1.5% sodium perborate + 1.5% $NaHCO_3$ + 1% boric acid, pH 7.7, 50°C, 30 min	0
Urea 6M + 1.5% sodium perborate + 2% boric acid, pH 8.3, 50°C, 30 min	+39
H_2O, pH 6.8, 50°C, 30 min	-3

Note: Bracketed treatments were run on adjacent membrane samples at the same time.

does not aid in the breakdown of the membrane deposit. It may even hinder the effectiveness of the sodium perborate.

To determine the effectiveness of urea and sodium perborate on full-scale modules, an attempt was made to clean modules operated under Phase V of Contract No. 14-12-181. The cleaning solution was circulated through the modules at approximately 4 gal./min during these tests. Results were as follows:

Module Data

6/10 No. 9 (Operated at Pomona approximately 5000 hr.)
Results on San Diego tap water at 600 psi: A* = 1.11×10^{-5}, 87.1% rejection. Original quality control test: A = 2.30×10^{-5}, 92.5% rejection. (10,000 ppm NaCl solution)

*A = water permeation coefficient (g/cm^2-sec-atm).

6/9 No. 14 (Operated at Pomona approximately 5000 hr.)
Results on San Diego tap water at 600 psi: A = 1.14×10^{-5}, 85.1% rejection. Original quality control test: A = 2.34×10^{-5}, 94.4% rejection.

6/10 No. 2 (Operated at Pomona approximately 5000 hr.)
Results on San Diego tap water at 600 psi: A = 1.24×10^{-5}, 85.0% rejection. Original quality control test: A = 2.42×10^{-5}, 94.1% rejection.

Cleaning Efforts

Module 6/10 No. 9 received circulating H_2O, pH 8.3, at 50°C for 1 hr. Results: A = 1.21×10^{-5}, 89.6% rejection on San Diego tap water. This treatment gave a 9% increase in water flow.

Module 6/9 No. 14 received a circulating solution of urea 6M, pH 8.3, at 50°C for 1 hr. Results: A = 1.30×10^{-5}, 81.4% rejection on San Diego tap water. This treatment gave a 14% increase in water flow.

Module 6/10 No. 2 received a circulating solution of 2% $NaBO_3 \cdot 4\ H_2O$, pH 10.2, at 50°C for 1 hr. Results: A = 1.44×10^{-5}, 45.8% rejection on San Diego tap water. This treatment gave a 16% increase in product water flow; however, it appears that membrane damage had occurred in the module.

Module 6/10 No. 9 (previously was given the hot H_2O treatment) received a urea 4M + 2% sodium perborate solution, pH 10.8, at 50°C for 1 hr. Results: A = 1.55×10^{-5}, 90.5% rejection on San Diego tap water. This treatment yielded a 20% water flow improvement.

New Membrane

New membrane was exposed to solutions of urea and sodium perborate at several pHs to determine the effect of the cleaning agent on rejection. The results, which are given in Table 5, indicate the need for pH adjustment to prevent membrane deterioration. This is essential when using the sodium perborate mixtures and is especially true when using solutions at elevated temperature. Fortunately, from results of the membrane cleanings it appears that good cleaning is possible with sodium perborate and urea at pH adjustments to 8.5 or lower. From the membrane test results it appears that there is no (or very little) membrane damage at this pH range and exposure time.

Other Results

The amount of experimentation that could be carried out on screening cleaning agents during the initial phase of this contract was limited by the number of available fouled modules. Fortunately, it was possible

TABLE 5
EFFECT OF CLEANING AGENT ON REJECTION

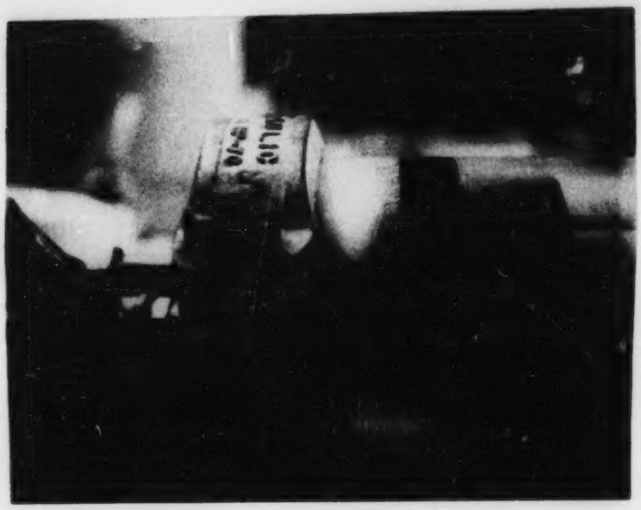
Treatment	Water Permeation Coefficient (g/cm^2-sec-atm x 10^5)	Percent Rejection	Salt Permeation Coefficient (cm/sec x 10^5)
Test Conditions: 10,000 ppm NaCl at 800 psi			
H_2O, pH 6.8, 22°C, 50 min	2.53	95.5	5.64
2% sodium perborate, pH 10.2, 22°C, 50 min	2.82	89.8	15.2
2% sodium perborate + 4% $NaHCO_3$, pH 8.7, 22°C, 50 min	2.60	94.8	6.60
Urea 6M, pH 8.2, 22°C, 60 min	2.37	94.7	6.22
Urea 4M + 2% sodium perborate, pH 10.8, 22°C, 60 min	2.73	92.4	10.2
H_2O, pH 6.8, 22°C, 60 min	2.81	95.0	6.85
2% sodium perborate, pH 10.2, 50°C, 50 min	2.41	39.8	187.3
2% sodium perborate + 4% $NaHCO_3$, pH 8.7, 50°C, 50 min	2.60	93.3	8.80
H_2O, pH 6.8, 50°C, 50 min	2.61	95.7	5.52
Urea 6M, pH 8.2, 50°C, 50 min	2.38	95.2	5.63
H_2O, pH 6.8, 50°C, 50 min	2.30	95.0	5.60
Urea 4M + 2% sodium perborate, pH 10.8, 50°C, 50 min	2.51	70.7	50.5
H_2O, pH 6.8, 50°C, 50 min	2.46	95.5	5.48
Test Conditions: 7,000 ppm NaCl at 800 psi			
Urea 6M, pH 7, 50°C, 60 min	1.86	96.4	3.01
	1.86	96.5	2.95
H_2O, pH 7, 50°C, 60 min	1.88	96.4	3.04
	1.80	96.7	2.73

to apply results obtained under OSW Contract No. 14-01-0001-2225(2) to selection of cleaning agents for operation on secondary effluent. In that study, small modules (3.5 ft^2) were operated on well-oxidized secondary effluent for several hundred hours. Membrane samples from the fouled modules were tested for water permeation before and after exposure to many different cleaners. The most promising cleaners were then applied to fouled modules and finally field tested. Results indicated that BIZ enzyme detergent, EDTA, and sodium perborate performed equally well in module cleaning. These cleaners were also selected for field evaluation under this study.

AIR-WATER FLOW DISTRIBUTION TESTS

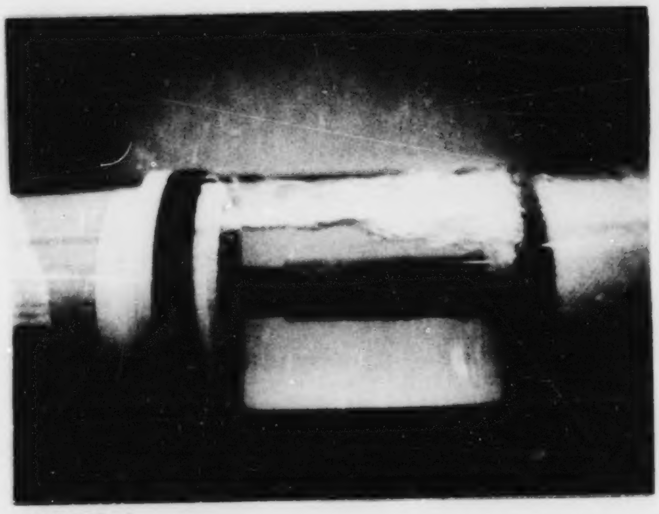
Air-water mixtures have previously been used to clean modules operated on municipal effluents. A series of exploratory tests was conducted to determine the air-water flow pattern. An acrylic vessel equipped with three 50-ft^2 spiral-wound modules was employed in the evaluation. Tap water and air were mixed at 60 psi before injection into the vessel. The flow rates were: water, 8 gal./min; air, 20 ft^3/min.

Figure 2 shows photographs of the air-water flow distributions that were observed using the test conditions described above. As can be seen in Fig. 2a, the air-water mixture coming out of the 1/2-in. feed tube shows relatively good mixing as it enters the first module. However, as Figs. 2b, c, and d indicate, after the air-water mixture has passed through the first module and on to the second and third modules, it has separated into two distinct layers. The air is flowing along the top of the pressure vessel, while the water flow is on the lower portion of the vessel. There is apparently some good air-water mixing within the modules since the air-water flow leaving the modules appears to have good mixing. This is probably the result of the brine channel spacer in the module, which has the polypropylene filaments placed on a bias with respect to the direction of the flow of the water. This brine spacer configuration provides additional flow turbulence in addition to being an aid in mixing the air and water.



M37303-1

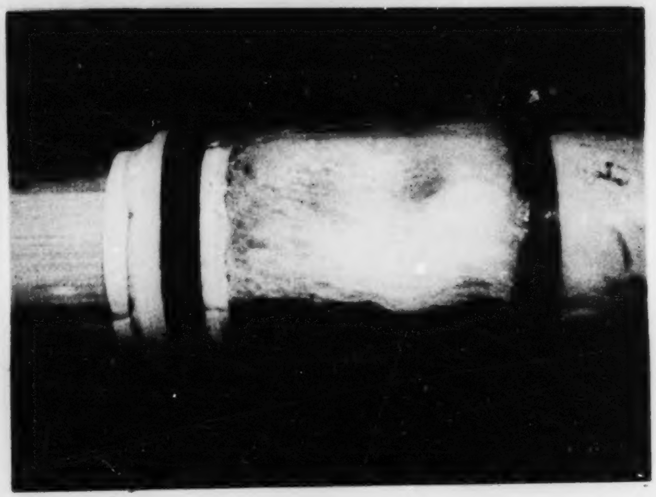
(a) Air-water mixture entering first module of acrylic vessel



M37302-1

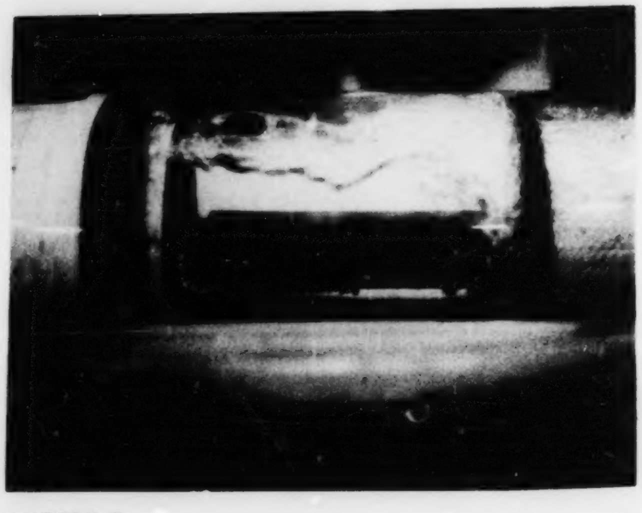
(b) Air-water mixture leaving first module and entering second module

Fig. 2. Air-water flow distribution test results



M37298-1

(c) Air-water mixture leaving the first module and entering the second module. Overhead view of the acrylic vessel



M37299-1

(d) Air-water mixture leaving the second module and entering the last module

Fig. 2. (Continued)

From these tests it appeared that the procedure being used for the Pomona air-water flush was not giving a good mixture. In view of the difficulty of mounting the vessels vertically, it was decided to suspend this flushing procedure. A 10 gal./min tap-water flush was substituted, which gave satisfactory field performance as described in Section V.

EFFECT OF CHLORINE ADDITION UPON MEMBRANE LIFETIME

Chlorine is almost always present in municipal water feed streams to reverse osmosis systems. Continuous low-level or periodic chlorine addition also offers an inexpensive and uncomplicated way of preventing biological growths on reverse osmosis membranes operating on sanitary waste feed streams. However, even low chlorine levels can cause deterioration of some reverse osmosis membrane materials. Polyamide membranes are particularly sensitive to chlorine and other oxidants. Tests were conducted under Contract No. 14-12-181(1) to determine the effect of chlorine exposure upon membrane lifetime. In that study, membranes exposed to approximately 2 mg/l chlorine for 29 weeks appeared to suffer some detrimental changes. However, the changes may have been due to excessive chlorine levels associated with a laboratory water and power failure after the eighth week.

Figure 3 is the flow diagram of the test apparatus for this experiment. The exposure levels included continuous 2 mg/l chlorine addition, a weekly intermittent chlorination of 10 mg/l for 60 min, continuous addition of chloroamines (2 mg/l chlorine and 10 mg/l ammonia), and a water control. Dechlorinated San Diego tap water with pH adjusted to approximately 5 was used as a feed. Enough membrane was used to permit four samples of each chlorinated and the control to be tested for water permeability and salt rejection each week. The ortho-tolidine test was used for control of the gas chlorinators, which were also periodically checked against starch-iodine titration. Figures 4 and 5 are linear plots indicating the performance during 190 days of exposure. The data collected indicate that chlorine exposures have had very little, if any, effect on the membrane properties at the levels and conditions tested.

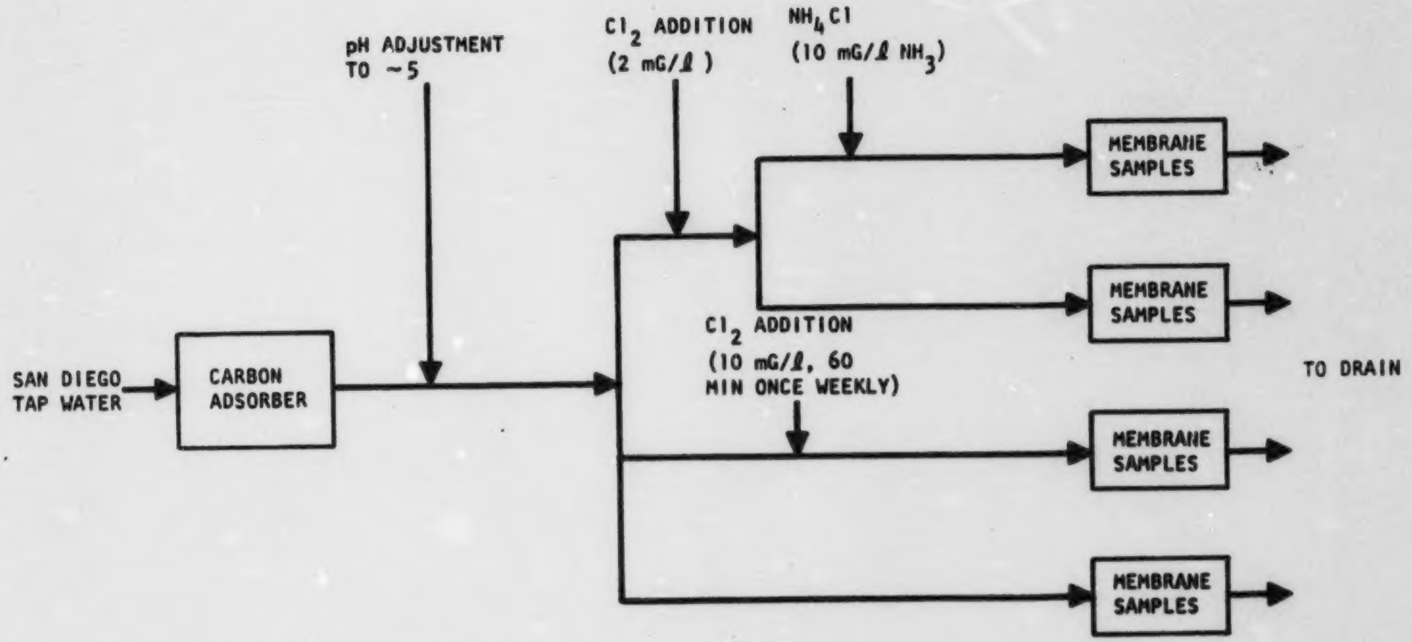

SAN DIEGO TAP WATER
CARBON ADSORBER
pH ADJUSTMENT TO ~5
Cl_2 ADDITION (2 mG/ℓ)
NH_4Cl (10 mG/ℓ NH_3)
Cl_2 ADDITION (10 mG/ℓ, 60 MIN ONCE WEEKLY)
MEMBRANE SAMPLES
MEMBRANE SAMPLES
MEMBRANE SAMPLES
MEMBRANE SAMPLES
TO DRAIN

Fig. 3. Membrane chlorination test flow diagram

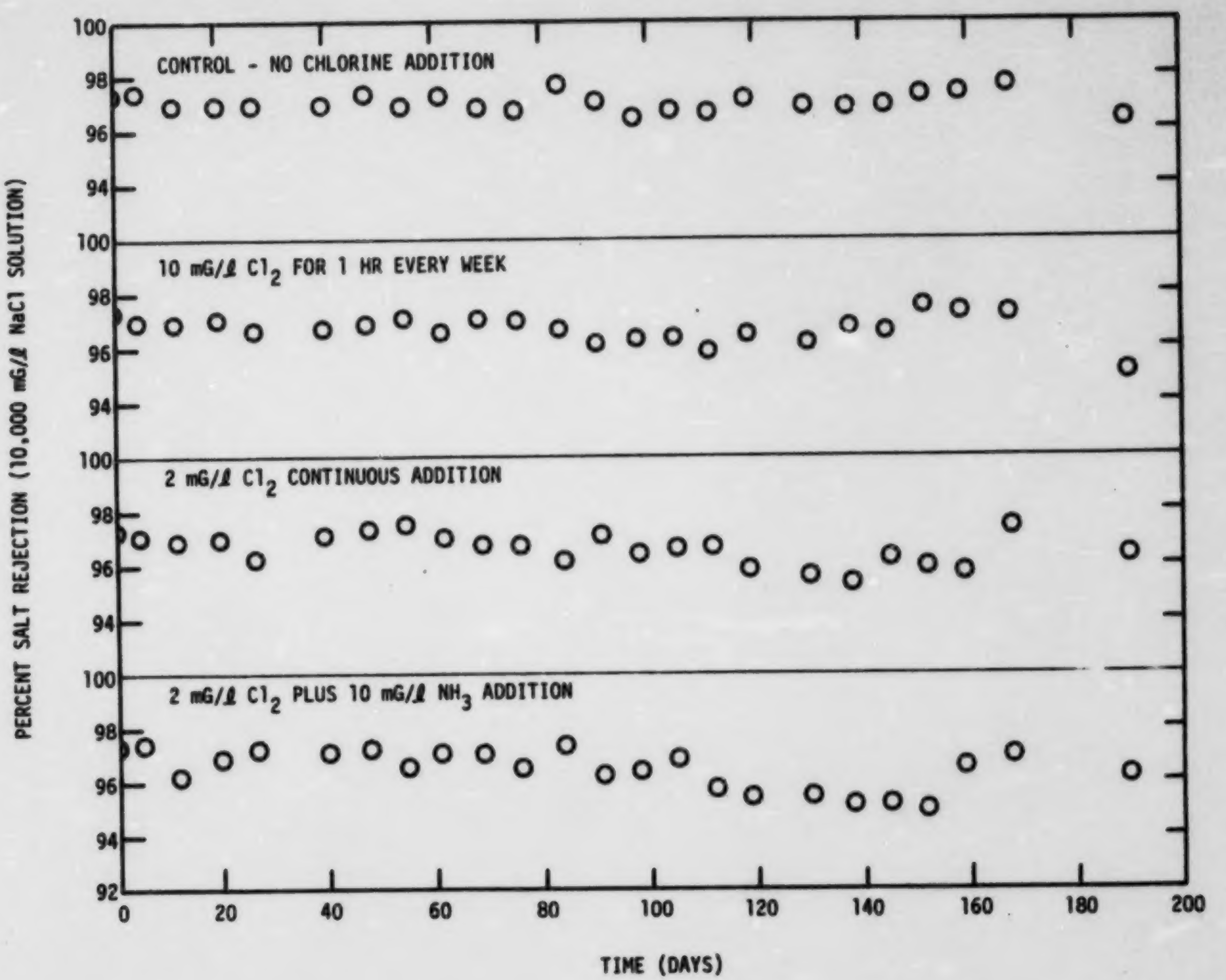


Fig. 4. Effect of chlorine addition on membrane salt rejection capability

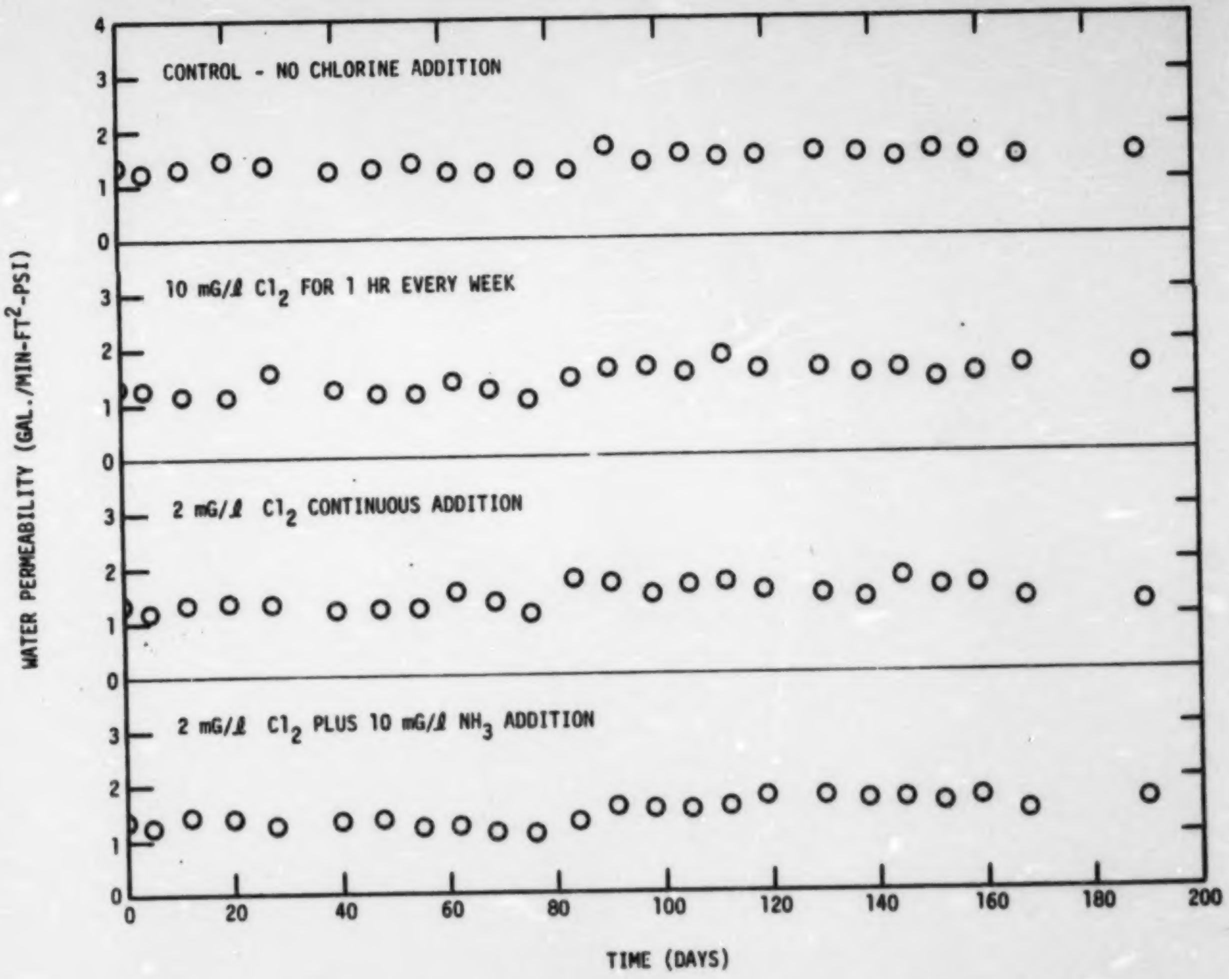


Fig. 5. Effect of chlorine addition on membrane water permeation

SECTION V
FIELD TESTS

Field testing was conducted at the Pomona, California Water Reclamation Plant of the County Sanitation District of Los Angeles. The Pomona plant is basically a conventional activated-sludge plant with enough design flexibility to permit variations in operation that make the effluent more suitable for tertiary processing. It is located adjacent to the major trunk sewer that conducts the wastes of the surrounding community to the central Los Angeles County system.

Raw sewage is pumped from the trunk sewer and is treated at the activated-sludge water reclamation plant, the effluent from which is used in a number of pilot plant studies. The treatment facilities operate under virtually constant hydraulic loading and with minimum variations in organic and nutrient loadings compared with conventional systems. This enables the Pomona plant to operate under relatively constant and probably optimum loading. Primary and waste secondary sludge are returned to the trunk sewer, and in case of deterioration in treatment for any reason, operation can easily be controlled to assure a rapid return to satisfactory conditions. The feeds for the reverse osmosis tests consisted of secondary clarifier effluent from the activated-sludge facility and the same effluent after it had been processed through a granular-activated-carbon adsorption system. Later the testing was expanded to include chemically clarified primary effluent with and without carbon adsorption processing.

DESCRIPTION OF PILOT PLANT UNITS

The two 10,000 gal./day spiral-wound reverse osmosis units employed under the previous contract were significantly modified during the initial stage of the present contract. Both units were equipped with piping and valves to direct cleaning or flushing solution through one pressure vessel at a time. There was also significant pretreatment modification.

Figure 6 is a schematic flow diagram of a modified unit. The effluent feed is treated with acid (pH 4 to 6) and gaseous chlorine and enters a 300-gal. mixing tank. It is then sand filtered and pressurized to the operating pressure. Pressure in the unit is controlled by an Apco backpressure regulator. Feed flows through the reverse osmosis unit, which consists of a 2-1-1 parallel series array of 4-in. Schedule 80 pipe pressure vessels that are 10 ft long and loaded with production-size ROGA spiral-wound reverse osmosis modules. Each pressure vessel contains three modules in series, so that a full loading consists of twelve modules.

In the reverse osmosis unit about 50% to 60% of the feed is converted to product water. The actual conversion or recovery varied throughout the test period because of improvements in membrane permeability and changes in operating pressure. Unconverted feed or brine leaves the last pressure vessel. A portion of the brine is recycled to the feed mixing tank, and the rest is discarded. Brine recycle is employed to raise the apparent water recovery of the unit to 75% to 80%, which is typical of a larger plant. This is necessary because concentration polarization limits the exit brine flow from any pressure vessel to a minimum of 4 gal./min. Recycle of the brine causes the feed concentration of salts and organic matter to rise. Thus, the unit operates as the latter section of a larger unit operating at 75% to 80% recovery. Membrane fouling is probably increased because of the greater concentrations of salts and organic matter present in the feed and throughout the unit. The test results should be representative of the worst case.

Pretreatment of the effluent feed varied throughout the test period. It was highly dependent upon the type of effluent and will be discussed later in this section.

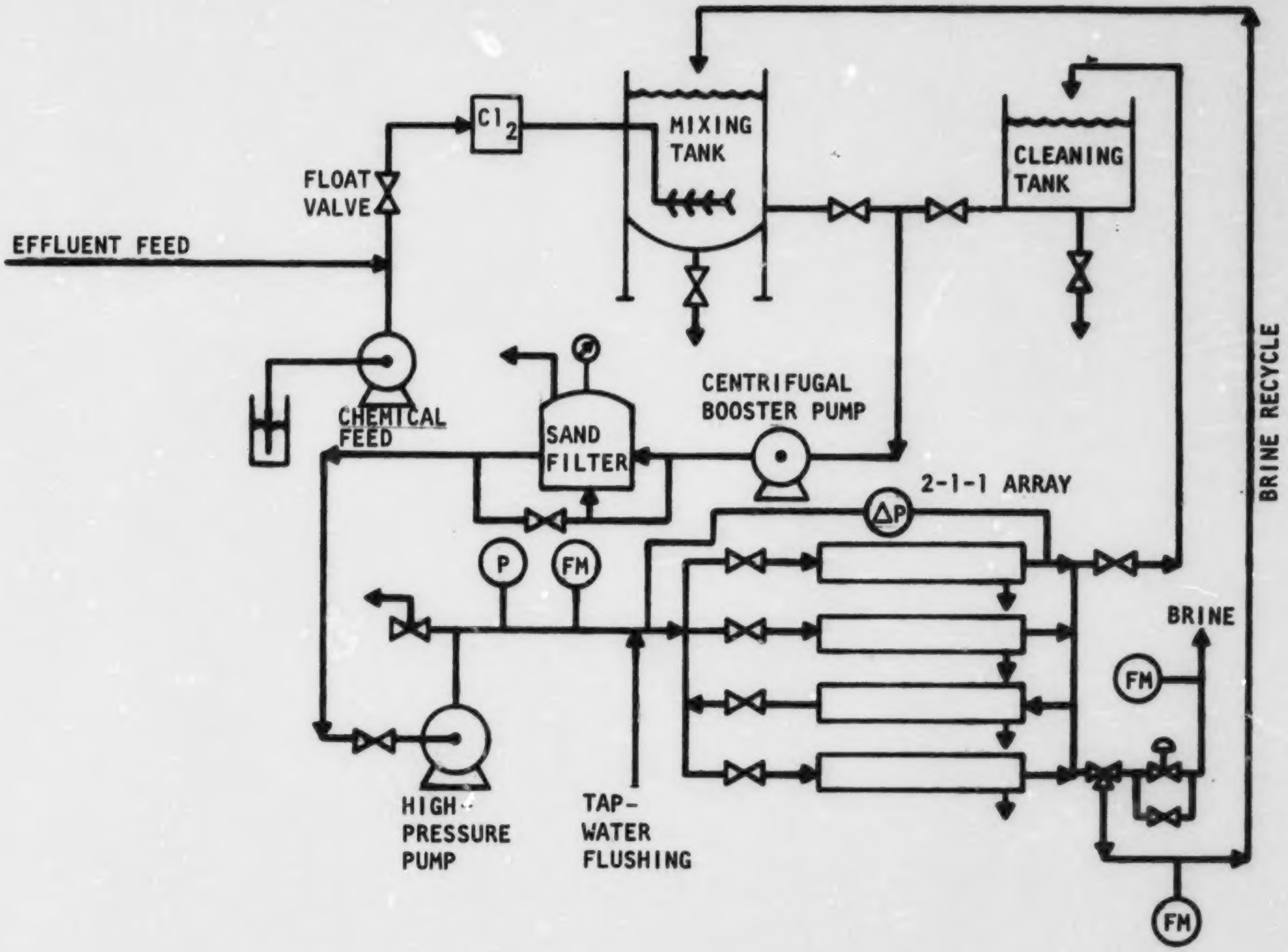

EFFLUENT FEED
FLOAT VALVE
Cl_2
MIXING TANK
CLEANING TANK
CHEMICAL FEED
SAND FILTER
CENTRIFUGAL BOOSTER PUMP
2-1-1 ARRAY
ΔP
P
FM
BRINE
FM
FM
BRINE RECYCLE
HIGH-PRESSURE PUMP
TAP-WATER FLUSHING

Fig. 6. Schematic of a Pomona field test unit

An experimental and cleaning unit was also constructed. It contains pretreatment provisions plus two parallel reverse osmosis systems. One system consists of a 10-ft long 4-in. diameter standard pressure vessel that accommodates three production spiral-wound modules. The other system, for studying several levels of operating parameters at the same time on the same feed, can accommodate up to twelve 5-ft^2 spiral-wound modules in parallel. Figure 7 is a schematic diagram of the experimental unit.

Sample valves were installed in each unit so that raw feed, pretreated feed, brine, and product streams could be sampled on a regular schedule. Instrumentation was included to measure temperature and pressure of the feed, pressure differential across each tube, and flow rates of the feed, brine, product, and brine recycle streams. Sulfuric acid was added to the feed by a proportional chemical feed pump. The amount was controlled by a pH controller. Gaseous chlorine was added to the feed by an Advance Gas Chlorinator.

All units were designed and constructed to be cleaned regularly without disassembly of manifolds and temporary hookups. A chemical cleaning solution was made up in the cleaning tank and was then circulated through each unit by a centrifugal booster pump. Enough valves were provided in the unit so that each tube could be cleaned individually or the unit could be cleaned as a series-parallel array. Tap water could be introduced for flushing just ahead of the pressure vessel array.

ACTIVATED-SLUDGE EFFLUENT PILOT PLANT TESTS

The purpose of the activated-sludge effluent reverse osmosis tests was to develop operating techniques that would permit product water fluxes of 8 to 10 gallons per square foot per day (gfd) without activated-carbon pretreatment. This goal was accomplished by improving operating and cleaning techniques. The ability to operate on activated-sludge effluent with only sand filtration, acid, and chlorine as pretreatment was demonstrated in a long-term test.

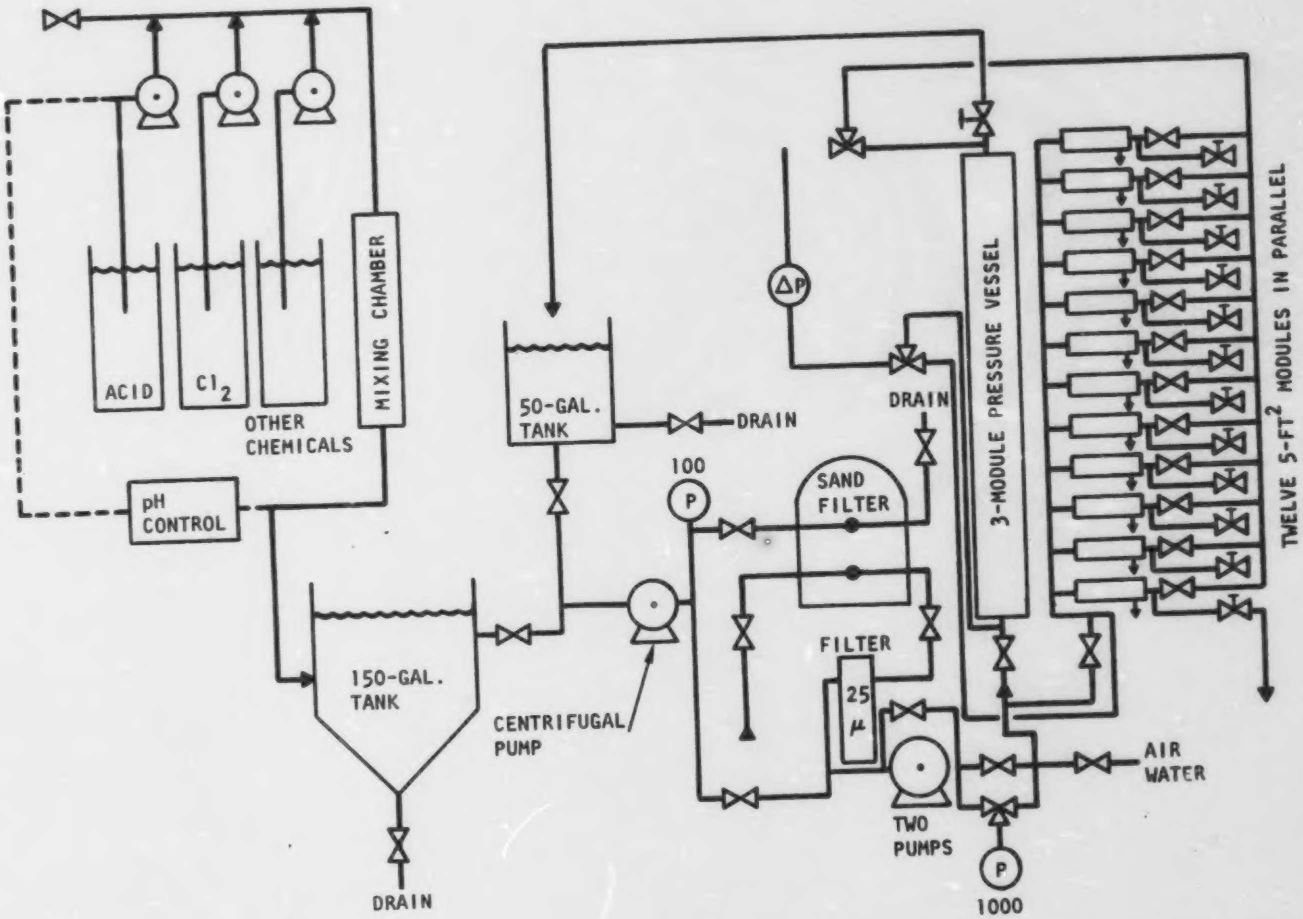

ACID
Cl_2
OTHER CHEMICALS
MIXING CHAMBER
pH CONTROL
50-GAL. TANK
DRAIN
150-GAL. TANK
DRAIN
CENTRIFUGAL PUMP
100
P
ΔP
SAND FILTER
FILTER
25 μ
DRAIN
TWO PUMPS
P
1000
AIR
WATER
3-MODULE PRESSURE VESSEL
TWELVE 5-FT^2 MODULES IN PARALLEL

Fig. 7. Schematic of experimental unit (trailer-mounted)

Pomona Phase V Field Test Data

Under the previous contract, No. 14-12-181, the two 10,000-gpd units were left running to demonstrate a "best effort" based on feed treatment, membrane type, spacers, and other parameters. In addition, there had been some evidence that warranted a systematic study of the value of vertically oriented pressure vessels to minimize fouling and/or enable more effective cleaning.

Both systems were plumbed in a 2-1-1 array, with the Unit I tubes horizontal and the Unit II tubes vertical. Both systems were to be operated in as nearly identical a manner as possible. Both units were loaded with high-flux modules with standard Vexar brine channel spacer and operated at 600 psi, with 4.5 gpm brine flow (3 gpm being recirculated) and a pH of 5.5 ± 0.5 adjusted with HCl. They operated initially on carbon-column effluent with weekly BIZ cleanings and daily air-water flushing.

At approximately 500 hr, it was decided to change the feed from carbon-column effluent to sand-filtered secondary effluent. Because of equipment limitations, the use of sand filters precluded the use of chlorine. Enzyme detergent cleaning was increased to twice weekly and the daily air-water flushing continued. The pH of the feed was adjusted with H_2SO_4 instead of HCl from this point on.

Unit II operated in this manner for only 100 hr before the contract and the run were terminated. The modules were removed and stored in Merthiolate solution. The value of vertically orienting the pressure vessels remains in doubt.

Unit I continued to operate after the contract termination under supervision of the Los Angeles County Sanitation District with minimal support from Gulf Environmental Systems. After the feed change at 500 hr, it was again changed at 770 hr to unfiltered chlorinated secondary effluent. The run was halted at 5200 hr due to pump failure, and the unit was flushed with tap water for

10 days. The unit ran again for 87 hr before the modules were discharged and stored in Merthiolate solution.

Figures 8 and 9 are plots of the salt rejection versus time for Units I and II. They show that although there was a considerable variation in rejection, caused mainly by leaking modules or connections and too-low pH adjustment, the rejection at the end of the run was essentially the same as at the beginning.

Figures 10 and 11 are log-log plots of the water permeability coefficient A versus time for both units. The rather severe flux declines experienced in the first 100 hr were caused by lack of acid addition and by effluent of extremely poor quality due to excessive suspended solids. Both units were flushed with acidified tap water (pH 3 to 6) for several days before operation was continued. Brine recirculation was discontinued due to pump failures, and the bulk of the operation time was at 3.0 gpm total brine flow.

A total of six modules were selectively removed at three times during the run as shown in Fig. 12 and replaced with modules from Unit II that had been stored. The replacements were necessitated by abnormally low rejections and/or water flux values. Inspection of all modules during these shutdowns revealed heavy deposits of "grease balls" and debris on the lead end of the modules as experienced previously. Also, a few brine seals had failed, probably due to the deposits, and one module had the outer tape wrap split open along the seam. This module was opened, and the membrane was found to be covered with a slimy material but the amount was less than had been present in other modules. There were areas of heavy fouling, indicating poor water circulation, and in these areas a granular deposit was found which was suspected to be phosphate. No further cleaning of the returned modules was attempted.

The unit was cleaned once with a warm 2% ammonium bifluoride solution following the usual BIZ cleaning. There was no significant difference in

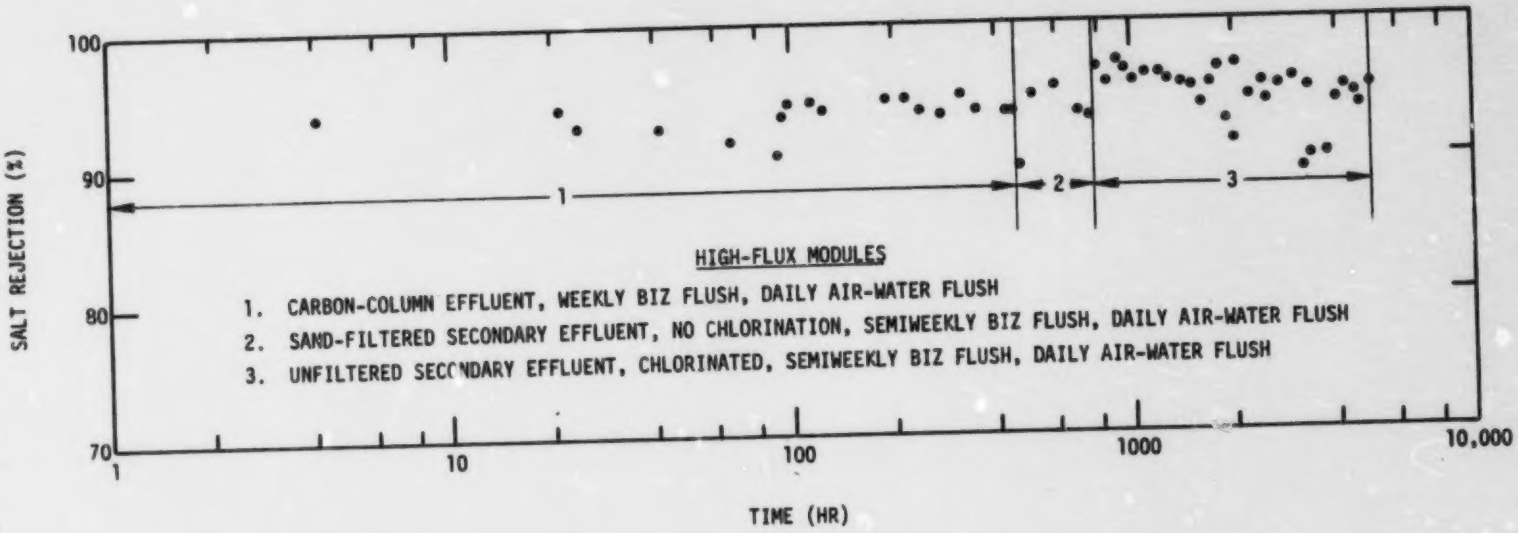


Fig. 8. Percent salt rejection versus time - Unit I, Phase V extension

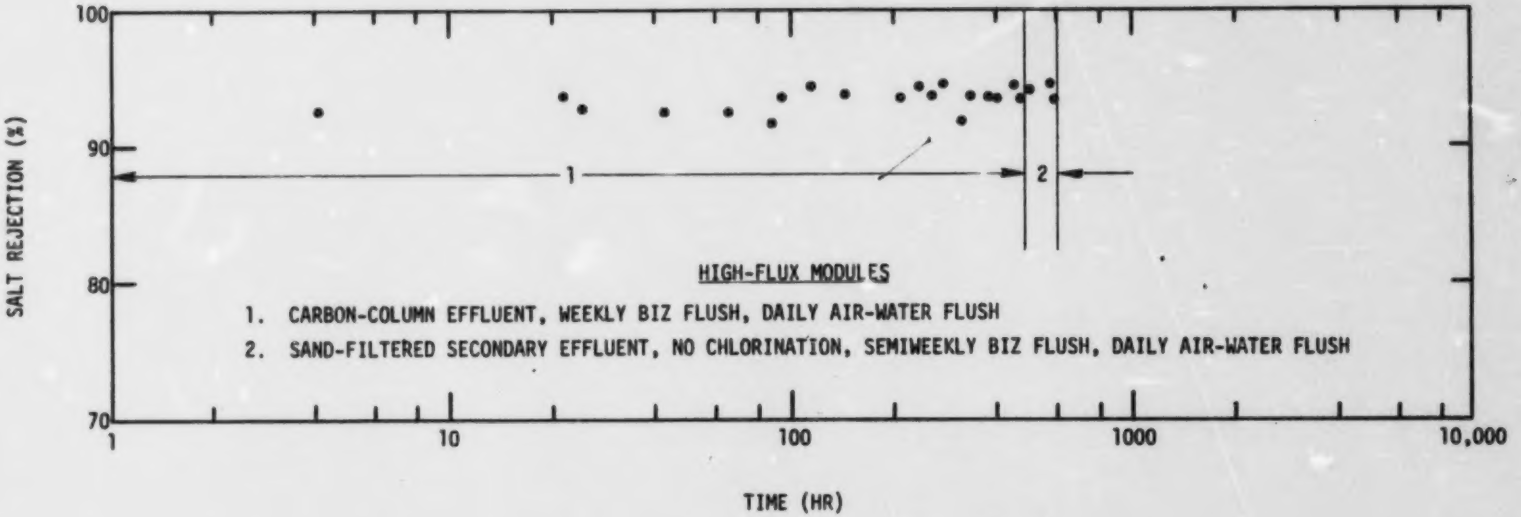


Fig. 9. Percent salt rejection versus time - Unit II, Phase V extension

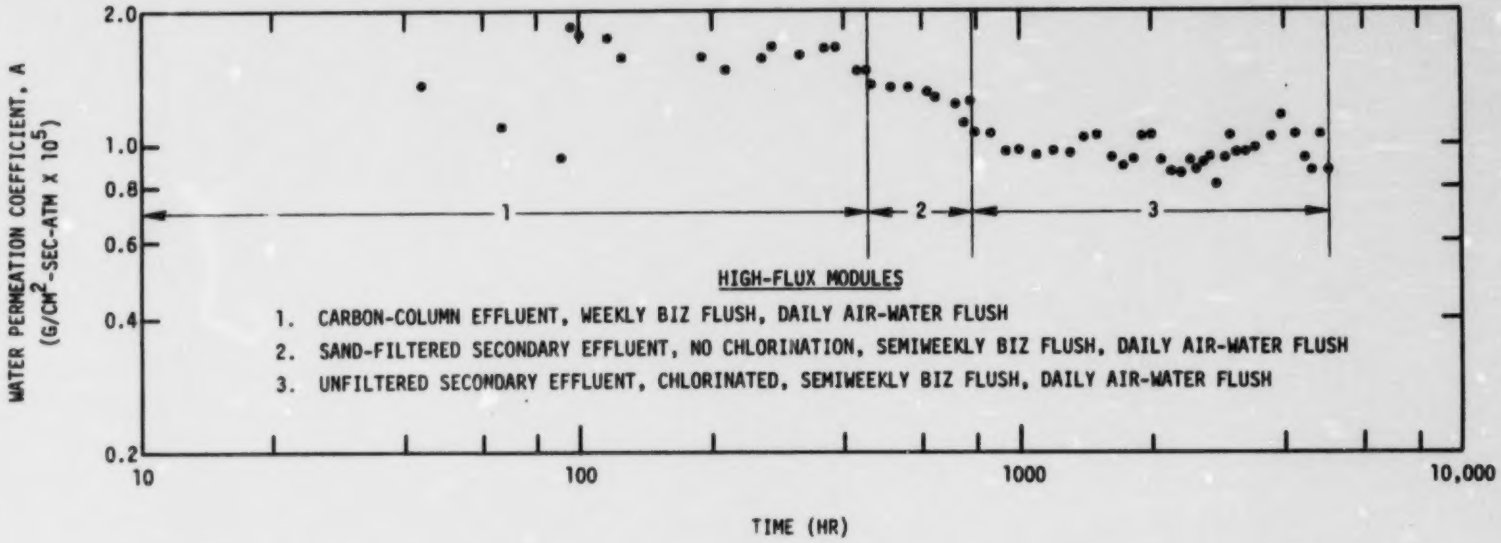


Fig. 10. Water permeation coefficient A versus time - Unit I, Phase V extension

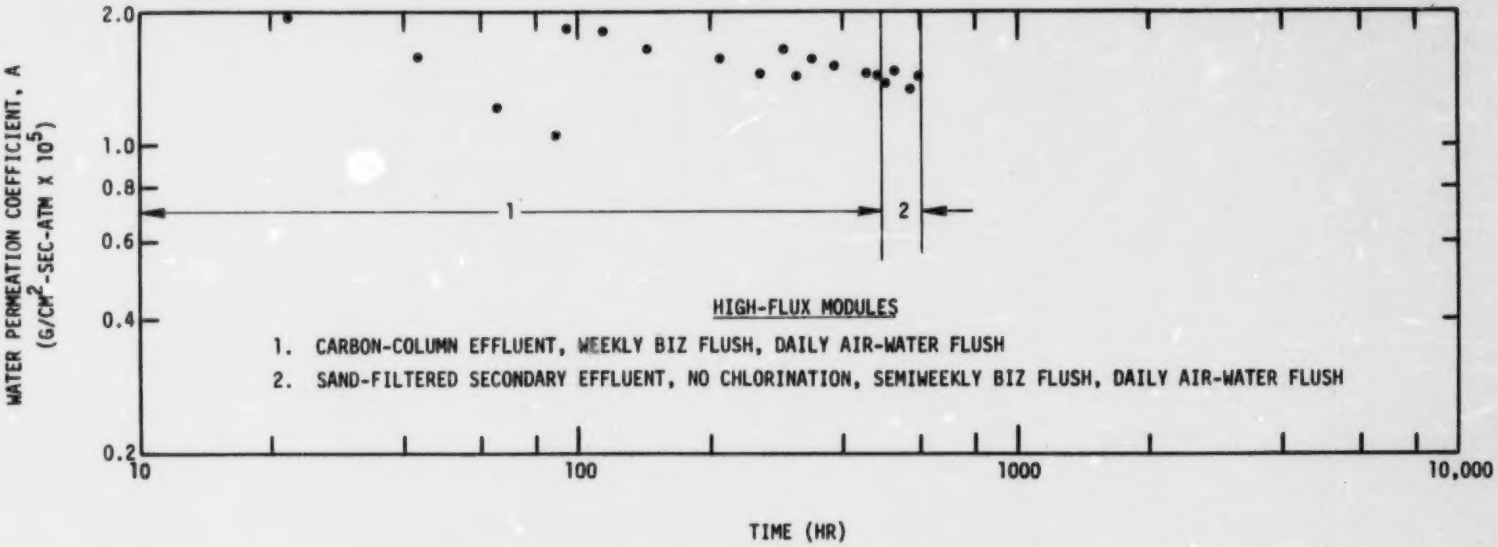
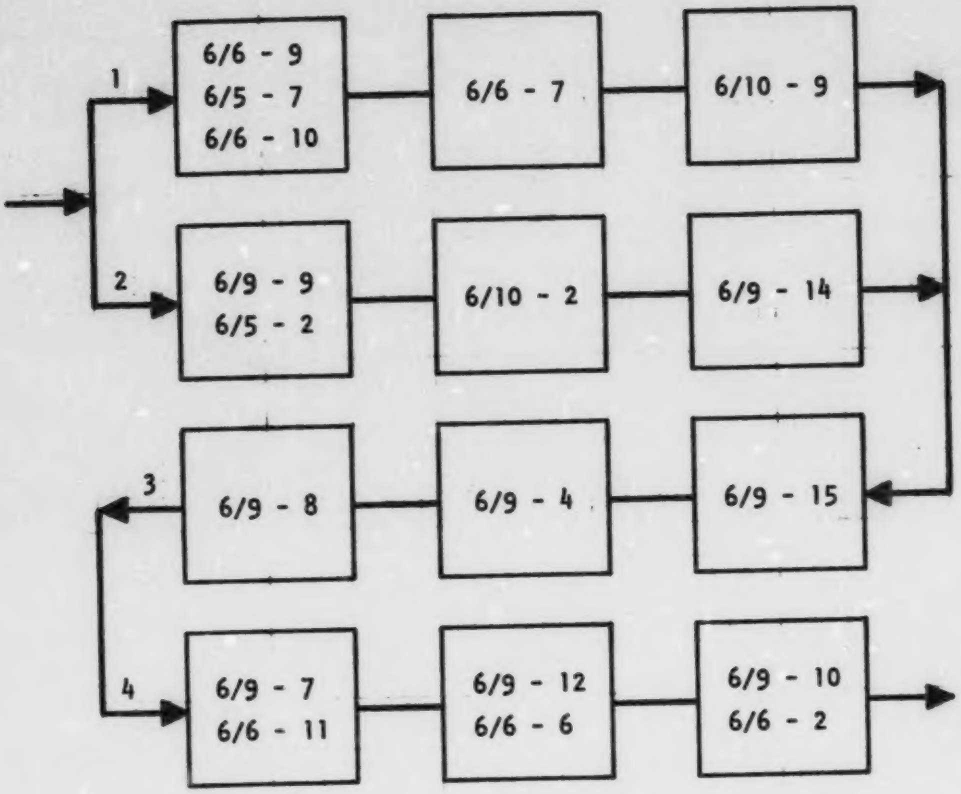


Fig. 11. Water permeation coefficient A versus time - Unit II, Phase V extension


1
6/6 - 9
6/5 - 7
6/6 - 10
6/6 - 7
6/10 - 9
2
6/9 - 9
6/5 - 2
6/10 - 2
6/9 - 14
3
6/9 - 8
6/9 - 4
6/9 - 15
4
6/9 - 7
6/6 - 11
6/9 - 12
6/6 - 6
6/9 - 10
6/6 - 2

9-2-69	REPLACED 6/6 - 9 WITH 6/5 - 7	1490 HR
	REPLACED 6/9 - 9 WITH 6/5 - 2	
11-6-69	REPLACED 6/5 - 7 WITH 6/6 - 10	2961 HR
12-16-69	REPLACED 6/9 - 7 WITH 6/6 - 11	3880 HR
	REPLACED 6/9 - 12 WITH 6/6 - 6	
	REPLACED 6/9 - 10 WITH 6/6 - 2	

Fig. 12. Loading arrangement for Unit I, Phase V extension

the two methods, although it was later discovered that the lead ends of the modules were partially plugged, suggesting poor circulation during cleaning.

In summary, Unit I accumulated 5287 hr with 7 of the original 12 modules in operation for the entire period. The water flux decreased from 15 gfd at 100 hr on carbon-column effluent feed to 11 gfd at 5000 hr. Although this decrease is excessive, this run demonstrated the ability to operate on unfiltered secondary effluent, often of rather poor quality with a large amount of heavy suspended solids, for over 4000 hr. These results indicated a baseline performance without sand filtration. The units were shut down after this test period, and the modifications described earlier in this section were made.

Experiment I - Activated-Sludge Effluent With and Without Activated-Carbon Pretreatment

The first experiment had two purposes: to determine the necessity of activated-carbon pretreatment; and to determine the effects of the equipment design and pretreatment modifications on the membrane fouling rate using the same cleaning procedure that was found to be effective under the previous contract. Unit I received carbon effluent feed, and Unit II operated on sand-filtered activated-sludge effluent. Model 4000 spiral-wound 50-ft^2 modules employing high-flux membrane cast on D-601 sailcloth backing, 0.045-in. polypropylene Vexar brine spacers, and melamine-treated tricot product water channels were used in both units. The flow diagram for Unit II was the same as shown in Fig. 6. Since Unit I operated on feed that had already passed through a series of activated-carbon columns, the sand filter was disconnected and the high-pressure feed pump drew water directly from the mixing tank.

Both units were operated continuously except for periodic shutdowns for water and cleaning solution flushing of the modules. The cleaning schedule was as follows:

Feed	Unit I Carbon-Treated Secondary Effluent	Unit II Secondary Effluent
Daily tap-water flush	5-min tap-water system flush, 5-min flush for each tube, 5 min system flush (30 min total), 10 gpm flow rate	Same
Cleaning	2% BIZ enzyme detergent, pH adjusted to 7.5-8.0, once weekly applied in the same way as the tap-water flush	Same solution twice weekly

The operating conditions for both units consisted of a feed pressure of 320 psig and 80% water recovery. The test duration was to be 1000 hr minimum. Each unit was initially operated at its natural recovery of approximately 50%, and the recovery was increased to 80% after the first chemical cleaning. Unit I initially produced permeate at a flux of 10.7 gal/ft^2/day with a water permeation constant of 2.44 x 10^{-5} g/cm^2-sec-atm and a conductivity rejection of 95%. Unit II initially (20 hr) produced permeate at a flux of 10.4 gfd with a water permeation constant of 2.38 x 10^{-5} g/cm^2-sec-atm and a conductivity rejection of 94.5%.

Figure 13 indicates the normalized* flux of the two units versus time. Flux decline with time would have been extremely great if the unit were not cleaned periodically. With cleaning, the product flux followed a sawtooth pattern with respect to time. The average flux decline was much lower and the operation of the unit became more economical. After a period of 300 to 400 hr, the decline of average flux with respect to time appeared to level off and a steady state was attained.

Arrows on Fig. 13 show when each unit was chemically cleaned. The enzyme detergent BIZ was used to clean both units during the first 1000 hr. After this period a mixture of 2% EDTA, 0.015% Triton X-100 non-ionic detergent, and 0.00015% carboxy methyl cellulose at pH 7.5 to 8.0 was used to clean Unit I. Both cleaners yielded good results.

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*Normalized permeate flux means that actual permeate flux data points were converted to the equivalent flux at 25°C. using a temperature correction factor shown in Reference 1.

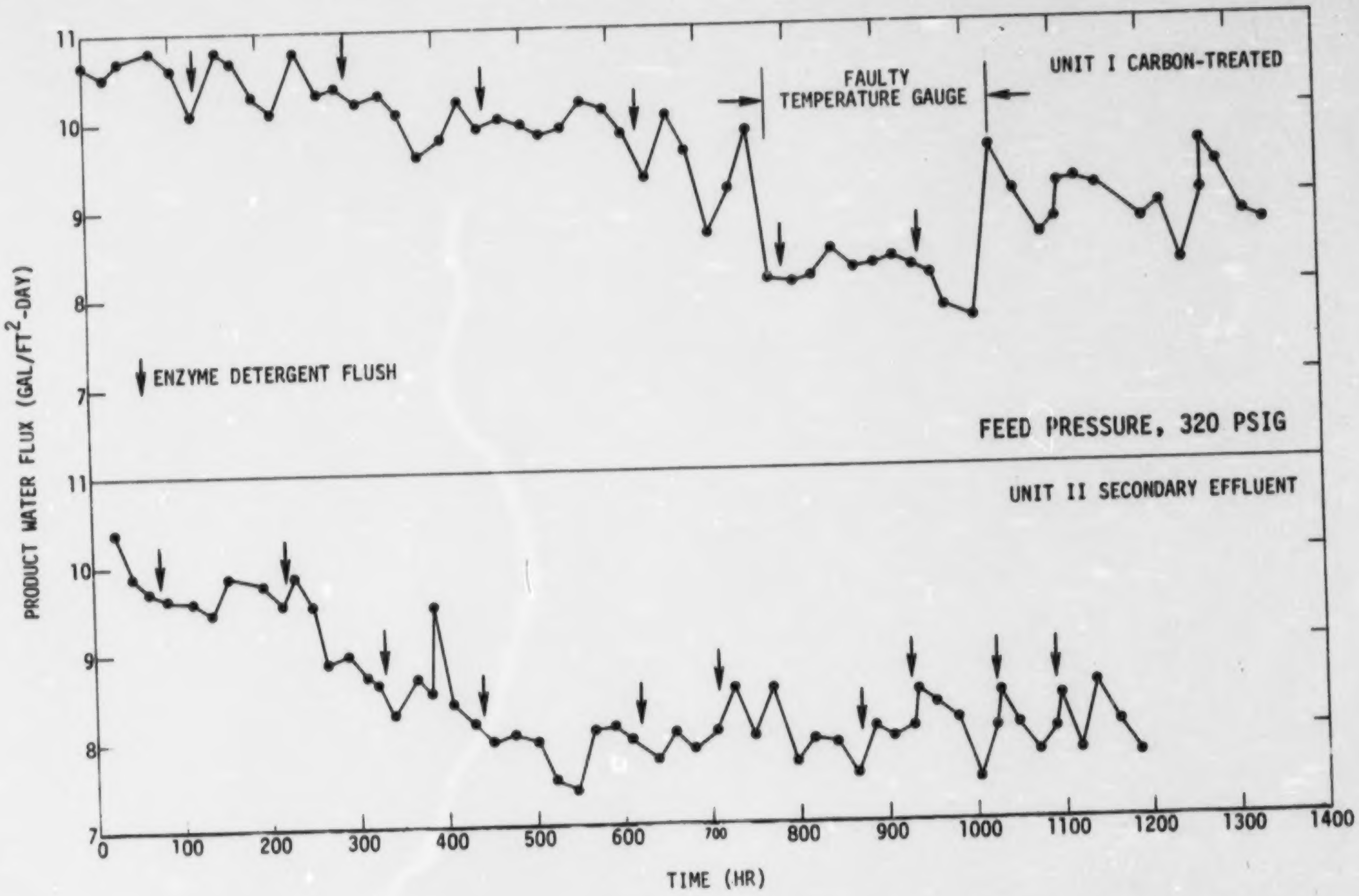


Fig. 13. Plots of product water flux versus time for Units I and II, Experiment I

Erratic temperature measurements somewhat clouded interpretation of Unit I data during the first 1000 hr. The gauge was found to be about 8°F in error after 760 hr. It was recalibrated at that time, and the normalized product flux dropped because of the temperature correction during the period 760 to 1000 hr. This drop was not observed in actual flow. From 1000 hr on, thermometer readings were used to normalize the data and the normalized flux rose again. In general, the actual product flow data were far less scattered than the normalized data. The temperature gauge was then replaced.

Unit I operated on carbon-treated secondary effluent, with a feed pressure of 320 psi and approximately 80% recovery, until the test was terminated at 1335 hr. Figure 14 indicates the variation of water permeation coefficient, normalized to 77°F, throughout the run. The log-log slope of this curve is -0.025 based on the best straight line by eye through the data points. This test has yielded the lowest flux decline slope to date for operation on carbon-treated secondary effluent at Pomona.

Unit II operated for 1184 hr on sand-filtered secondary effluent with a feed pressure of 320 psi and approximately 80% recovery. Figure 15 shows the variation of water permeation coefficient, normalized to 77°F, throughout the run. The log-log slope of this curve is -0.037 based on the best straight line by eye through the data points. This was the lowest flux decline slope ever achieved for operation on secondary effluent at Pomona. It is significantly lower than the flux decline slope of -0.055 achieved during a 9475-hr test conducted by the Los Angeles Sanitation District on carbon-treated secondary effluent. During this test with Unit II, the product water flux appeared to level off after about 500 hr of testing. Thus, one might expect that the log-log slope would tend to flatten in a longer run.

Figure 16 shows how the feed total COD varied throughout the experiment for Units I and II. In comparing Figs. 13 and 16, it appears that the product water flux declined more rapidly when the feed COD increased from the 20 to 30 range to the 60 to 70 range at around 250 hr.

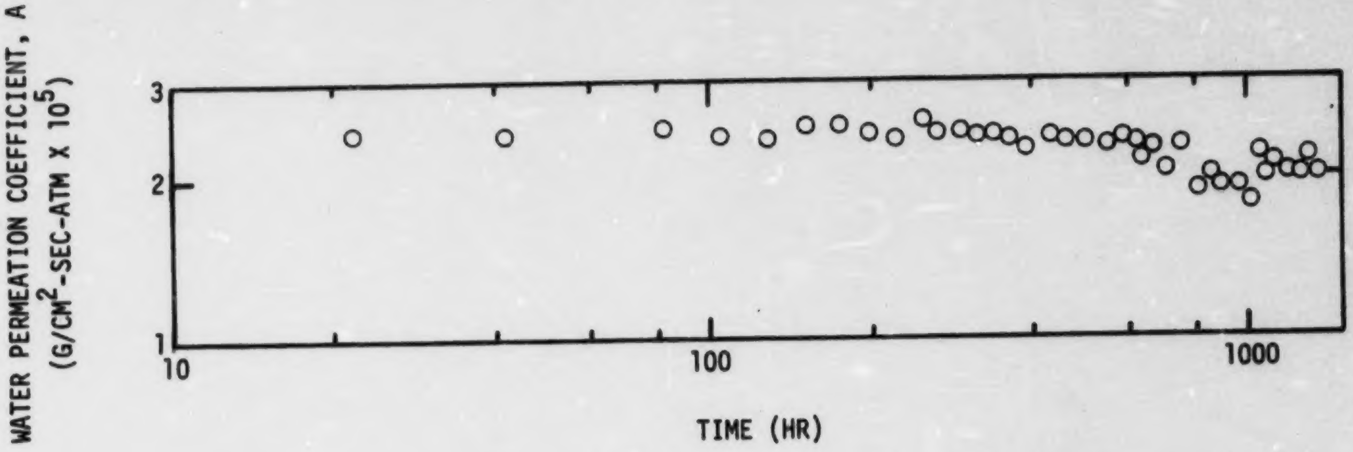


Fig. 14. Unit I: carbon effluent water permeation coefficient versus time - Experiment I

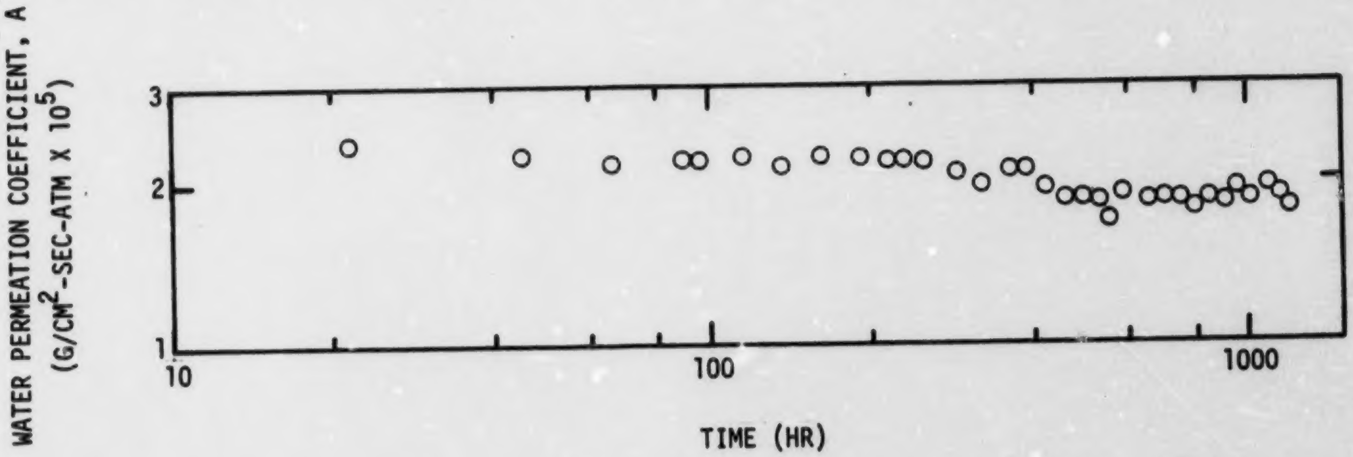


Fig. 15. Unit II: secondary effluent water permeation coefficient versus time - Experiment I

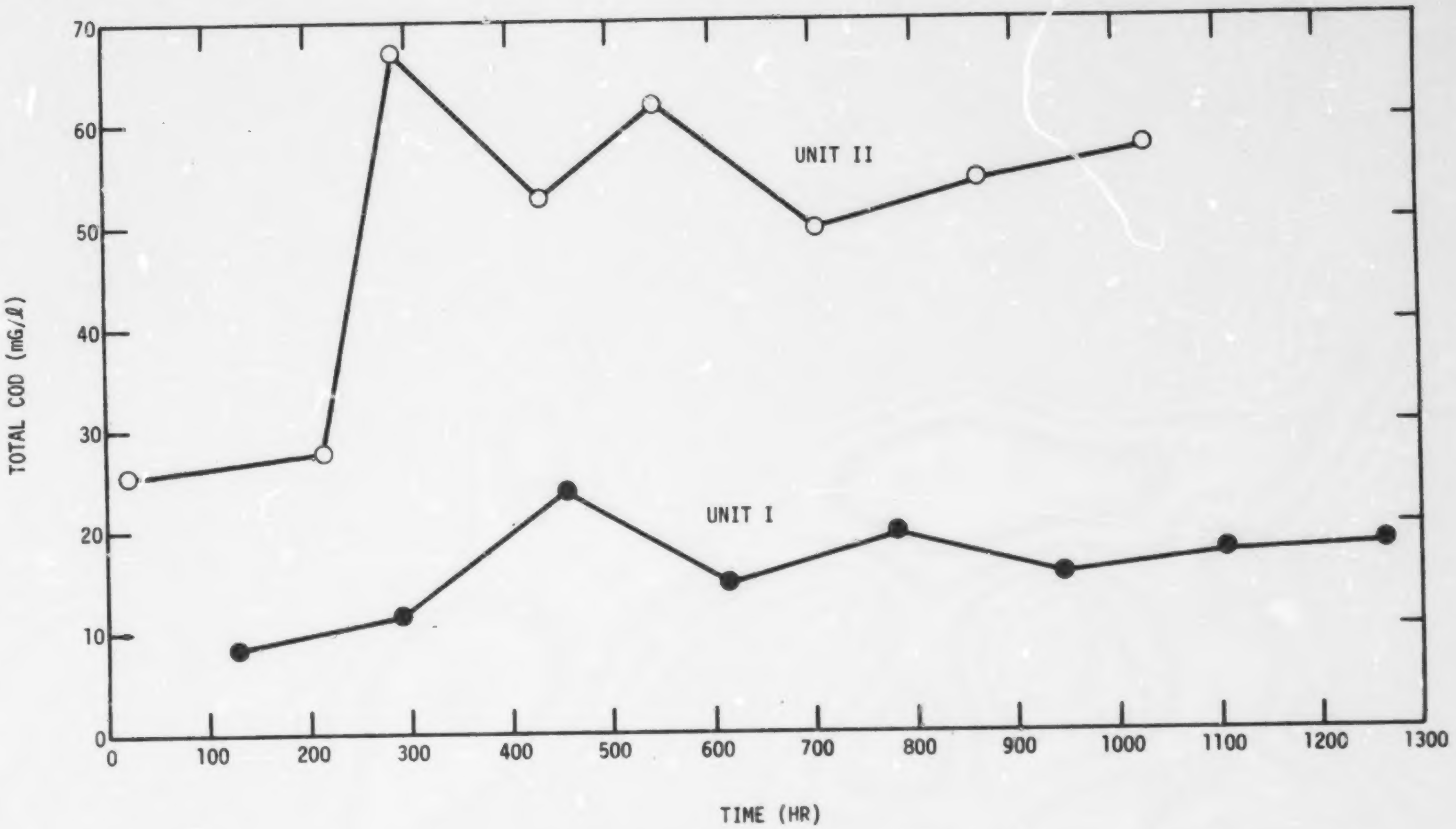


Fig. 16. Total chemical oxygen demand versus time for Unit I and II feed streams - Experiment I

Figure 17 indicates the time variation of feedwater turbidity throughout the first experiment. In contrast with the COD results, there appears to be little or no correlation between treated-feed turbidity and permeate flux. The treated-feed turbidity was higher than the raw-feed turbidity in almost all cases. This was probably due to two factors: recirculation of the brine and the effect of acid addition.

Other characterization measurements made during the first experiment are shown in Table 6. Silting indices had little value in predicting the fouling tendency of the feedwater because the carbon treated feed had a higher silting index. On the other hand, UV absorbance, TOC, and COD appeared to be better correlating parameters.

Figure 18 is a graph of the salt (conductivity) rejection behavior for Units I and II. Both units started with a rejection close to 95% and the rejection slightly increased during the test period. Percent reductions of the more important substances associated with pollution are shown in Tables 7 and 8. Chemical oxygen demand and phosphate rejections were excellent. Ammonia nitrogen rejections were very good. The tabulation of secondary effluent data includes Experiments I and II.

After the run was finished, two modules (4310 and 4326) from Unit II were opened and membrane deposit samples were taken for analysis. Both of these modules exhibited about the same degree of fouling. The fouling material removed was dark brown in color and appeared to contain a large amount of water. The amount of deposit present in these modules appeared to be less than the amount found in previous studies at Pomona. The deposit was definitely less tenacious. Both inorganic and organic analyses of this deposit were performed, as described in Section IV. Figure 19 is a photograph of the fouled membrane surface.

The pattern of the fouling was the same as the pattern of the brine spacer. One of the returned carbon-treated modules (4321) from Unit I was opened.

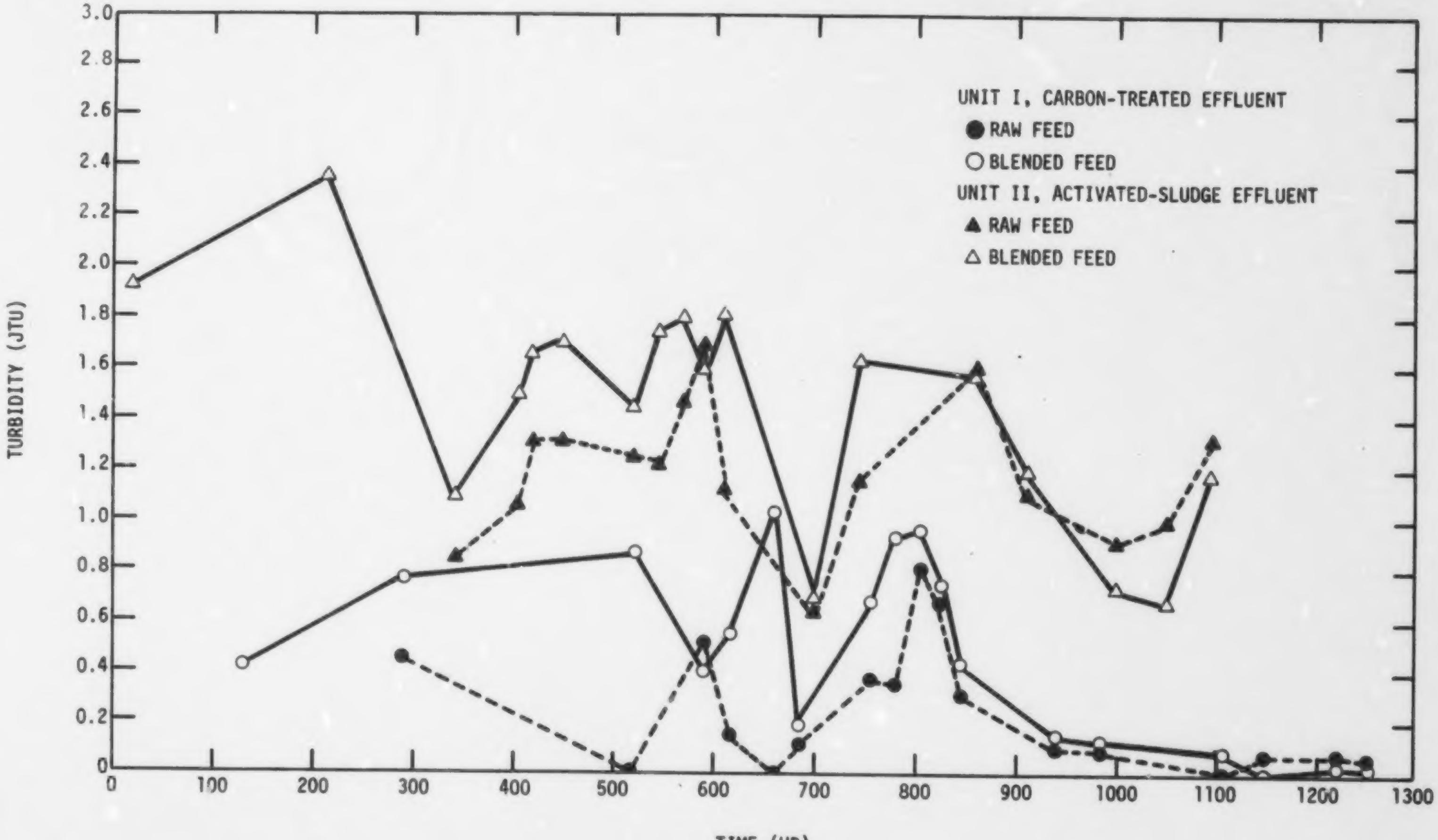


Fig. 17. Unit I and II feedwater turbidity versus time - Experiment I

TABLE 6
STREAM CHARACTERIZATION DATA - EXPERIMENT I

Date	Stream Sampled	pH	Turbidity (JTU)	Silting Index, No. 4 Orifice, 20 psi	UV Absorb. at 275 mμ	TOC (mg/1)
8/20/70	Secondary effluent	7.3	1.1	0.7	0.130	16.5
	Unit I					
8/20/70	After carbon treatment	7.3	0.6		0.030	8.5
8/20/70	After acid and chlorine addition	7.2	1.0		0.050	7.5
8/20/70	Permeate	4.2	0.08		0.005	2.0
8/20/70	Concentrate	3.8	1.8		0.100	12.5
	Unit II					
8/20/70	After acid and chlorine addition	3.8	2.6	0.7	0.195	19.5
8/20/70	After sand filtration	3.6	1.6	0.6	0.179	17.5
8/20/70	Permeate	4.3	0.07	0.05	0.006	2.0
8/20/70	Concentrate	3.1	3.5	1.3	0.375	38
8/26/70	Secondary effluent	7.0	2.5	1.2	0.119	
	Unit I					
8/26/70	After carbon treatment	7.1	1.0	1.4	0.029	
8/26/70	After acid and chlorine addition	3.2	1.8	0.88	0.050	
8/26/70	Concentrate	3.2	4.3	1.8	0.100	
8/26/70	Permeate	3.9	0.30	0	0.009	

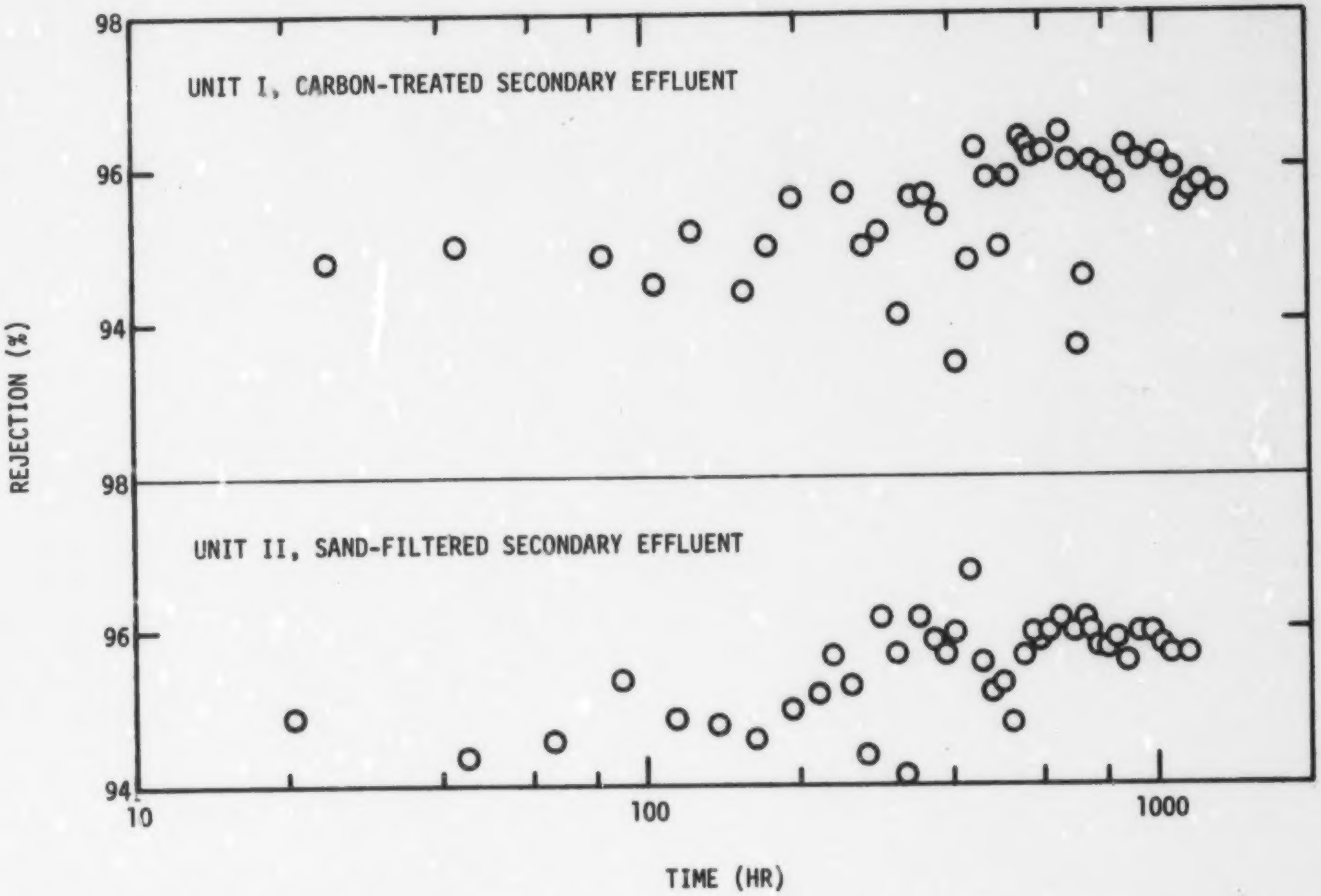


Fig. 18. Unit I and II salt rejection versus time, based on conductivity measurements - Experiment I

TABLE 7
REDUCTION OF FEED SOLUTES FOR CARBON-TREATED SECONDARY EFFLUENT(a)

	Feed,(a) Average (mg/l)	Permeate, Average (mg/l)	Percent Reduction(b)
Calcium	104	0.46	99.6
Magnesium	22.7	0.08	99.6
Sodium	198	14.7	92.6
Potassium	20	1.4	93
Ammonia-N	14.1	0.47	96.7
Chloride	221	15	93.2
Sulfate	379	1	99.7
Phosphate	59	0.06	99.9
Total COD	16.1	1.4	91.3
Dissolved COD	11.6	0.8	93.1
TDS	1206	57	95.3

(a) Based on small number of samples.

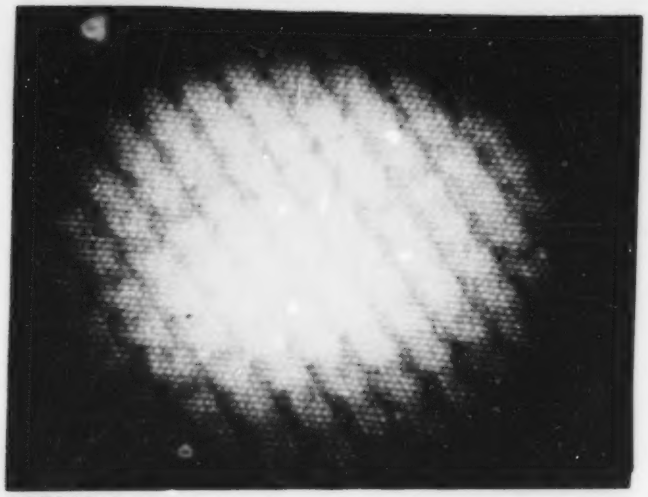
(b) Based on feed concentration.

TABLE 8
REDUCTION OF FEED SOLUTES FOR SECONDARY EFFLUENT

	Feed (mg/l)(a)		Permeate (mg/l)		Percent Reduction(b)
	Average Value	Range	Average Value	Range	
Calcium	92	62-160	0.33	<0.1-1.0	>99.6
Magnesium	20.6	14-31	0.1	Nil-0.18	>99.5
Sodium	177	99-310	10.6	7-18.2	94
Potassium	20.6	11-35.2	1.1	Nil-2.3	94.7
Ammonia-N	20.6	8.4-34	1.0	Nil-1.5	95.1
Chloride	159	94-315	8.6	6-15	94.6
Sulfate	422	220-852	1.9	Nil-6	>99.5
Phosphate	29.8	10.1-95	0.1	Nil-0.24	>99.7
Total COD	45.9	25.6-83.3	1.8	Nil-5	>96.1
Dissolved COD	38.1	16.9-72.3	1.5	Nil-5	>96.1
TDS	1123	751-1977	54	27-107	95.2

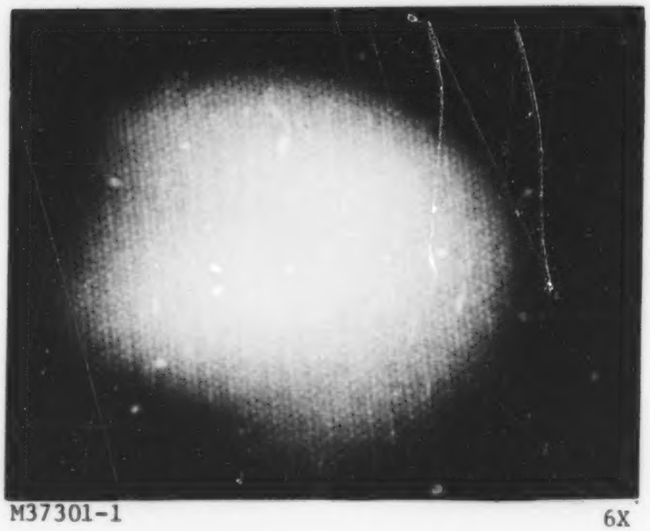
(a) Feed is sand-filtered activated-sludge effluent and contains recycled brine.

(b) Based on feed concentration.



M37300-1 6X

(a) Module 4305, operated 1184 hr on sand-filtered secondary effluent



M37301-1 6X

(b) Clean membrane surface

Fig. 19. Comparison of secondary-effluent-fouled membrane with clean membrane surface

The membrane surface was very clean, and it was impossible to collect enough material for a deposit analysis. There appeared to be no membrane fouling except for a small $CaSO_4$ deposit in the area closest to the product tube.

Membrane samples were taken from this module and were tested on 10,000 ppm NaCl at 800 psi. Results of this test for "as-removed" samples and membrane samples that received a 5-min ultrasonic cleaning were as follows:

Uncleaned(a)		Ultrasonically Cleaned(a)	
A	% Rejection	A	% Rejection
2.30	94.8	2.37	94.8

(a) Two-sample average

The data indicate that there is no or very little difference in the samples.

The other module (4352) was tested on 1000 ppm NaCl at 600 psi, and performed as follows: A = 2.02; percent rejection = 96.3. Original quality control test data on 2000 ppm NaCl at 600 psi gave the following results on this module: A = 2.00; percent rejection = 96.3. From these data it appears that this module experienced very little flux decline after 1300 hr of operation at 320 psi.

Results from Experiment I clearly indicated that activated-carbon pretreatment is not necessary for successful reverse osmosis operation on secondary effluent. Thus, a substantial cost saving can be achieved by replacing activated-carbon pretreatment with sand or graded media filtration. For this reason, the rest of the experimental program was concentrated on applying reverse osmosis to secondary and primary effluents. From comparison of the secondary effluent results obtained in Experiment I and Phase V, it was concluded that the pretreatment and operational changes were very beneficial with respect to maintenance of the permeate flux.

Experiment II - Activated-Sludge Effluent

The purpose of the second experiment was to compare the cleaning effectiveness of EDTA, sodium perborate, and BIZ enzyme detergent when operating on sand-filtered activated-sludge effluent. Both units received the same feed and were loaded with Model 4000 spiral-wound, 50-ft^2 modules. The process flow diagram for the experiment was the same as shown in Fig. 6. A 1000-hr minimum test period was scheduled. Recirculation was employed to operate at approximately 80% recovery, and the feed pressure was adjusted to yield an initial permeate flux of 13 gfd.

Both units were operated continuously except for periodic shutdowns for water and cleaning solution flushing of the modules, for pump repair, etc. The cleaning schedule was as follows:

	Unit I	Unit II
Daily flush	5-min tap-water system flush, 5-min flush for each tube, 5-min system flush	Same
Bi-weekly flush	2% EDTA, 0.015% Triton X-100 with 1% CMC (based on detergent weight), pH 7.5-8.0	2% sodium perborate, 0.015% Triton X-100 with 1% CMC (based on detergent weight), pH 7.5-8.0

Operating conditions for both units consisted of 550-psi pressure and an initial recovery of 77%. The recovery dropped to 67% after 100 hr and remained at that level for both units throughout the remainder of the experiment.

Figure 20 is a linear plot indicating the variation of permeate flux with time for both units, normalized to 77°F, throughout the run. Arrows indicate when the units were cleaned. Unit I was cleaned primarily with EDTA, while Unit II received a sodium perborate flush. Both units received several BIZ cleanings. As can be seen in Fig. 20, unit shutdowns as well as low-pressure operations accounted for significant permeate flux increases.

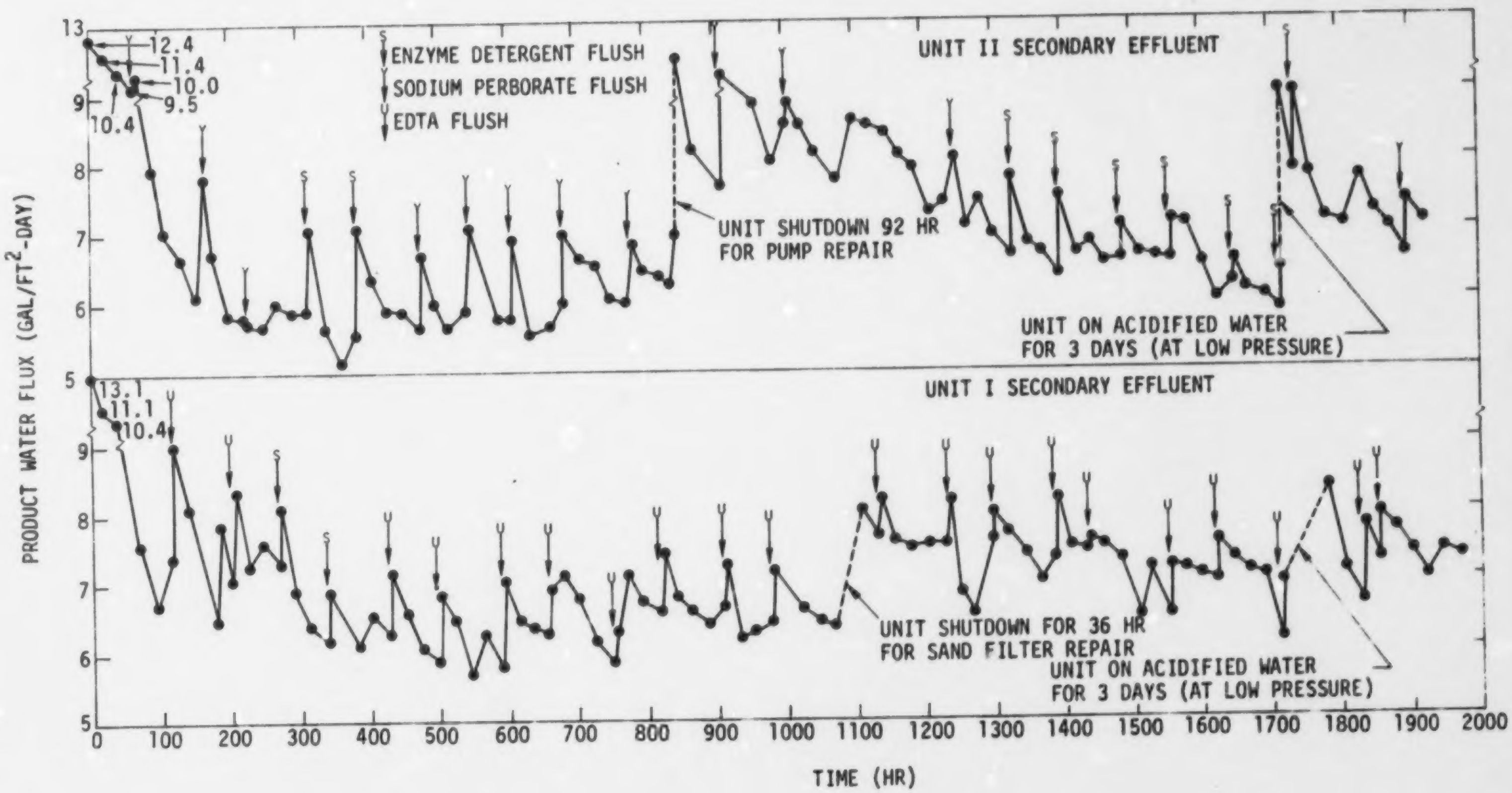


Fig. 20. Experiment II: permeate flux versus time (550 psig feed pressure)

Figures 21 and 22 also indicate the variation in permeation coefficient for Units I and II, respectively. The data were plotted on log-log paper for a determination of fouling slopes; however, the points did not follow a straight line. Therefore, fouling slopes for the 2000-hr second experiment could not be accurately obtained. However, the data from Unit I do show a stability in permeate flux after approximately 100 hr, indicating no fouling slope. The data points in Fig. 22 for Unit II are confounded by two large increases in permeate production when the unit was operated at low pressure. Because of this variation in the performance of Unit II and the prolonged stability of Unit I, meaningful fouling slopes for the second experiment cannot be obtained.

Unit II was shut down for pump repair for 92 hr after a run time of 850 hr. Chlorinated tap-water flushing during that period restored the product water flux to within 12% of the initial flux. After the unit was started, the flux declined, but not as rapidly as it did initially. This behavior is interpreted as evidence that fouling, not compaction, is responsible for the greatest part of the initial flux decline at these pressures. It is unlikely that the elastic component of membrane compaction could account for this flux recovery.

The experimental facts suggested a model in which the fouling layer forms a dynamic membrane in series with the cellulose acetate membrane. This membrane has some salt rejection characteristics and is easily compacted under pressure and difficult to clean even by chemical means. However, it is possible to clean it by prolonged flushing at low pressures.

The second experiment was continued beyond the 1000-hr completion to determine the steady-state flux on Unit II after the 92-hr shutdown. Both units were deliberately shut down for 3 days at approximately 1700 hr. The permeate flux rose significantly.

Figures 20, 21, and 22 all indicate the rate of permeate flux decline over the 2000 hr of the second experiment. As can be seen from the data in these

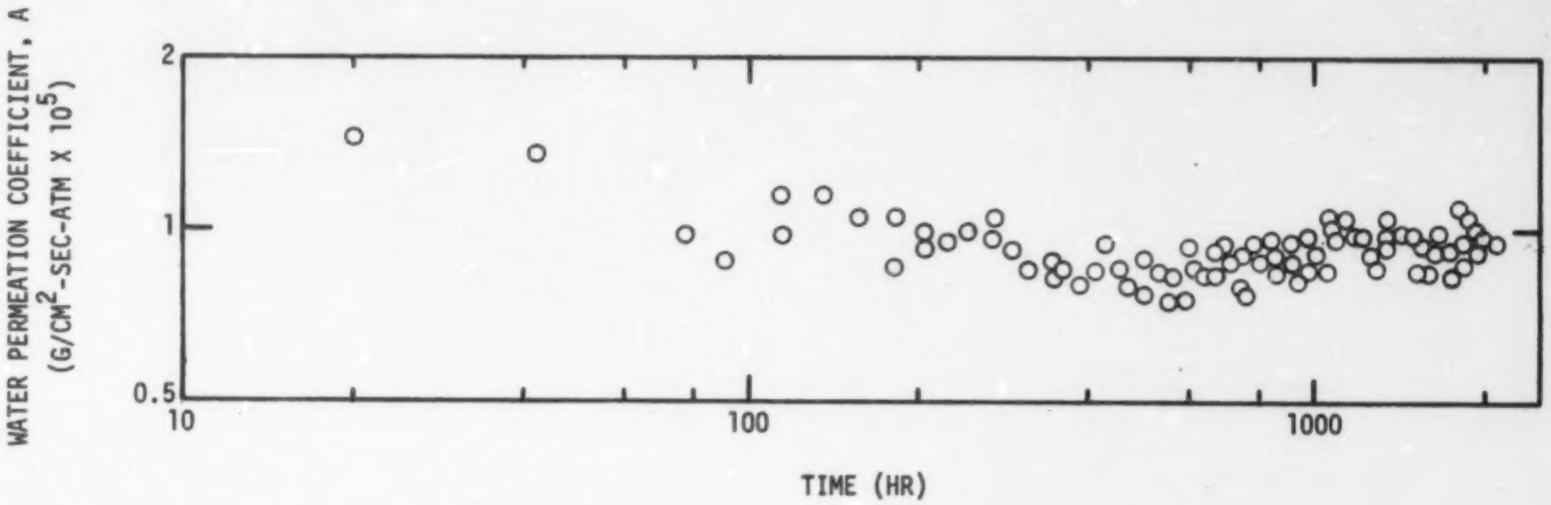


Fig. 21. Unit I: secondary effluent water permeation coefficient versus time - Experiment II

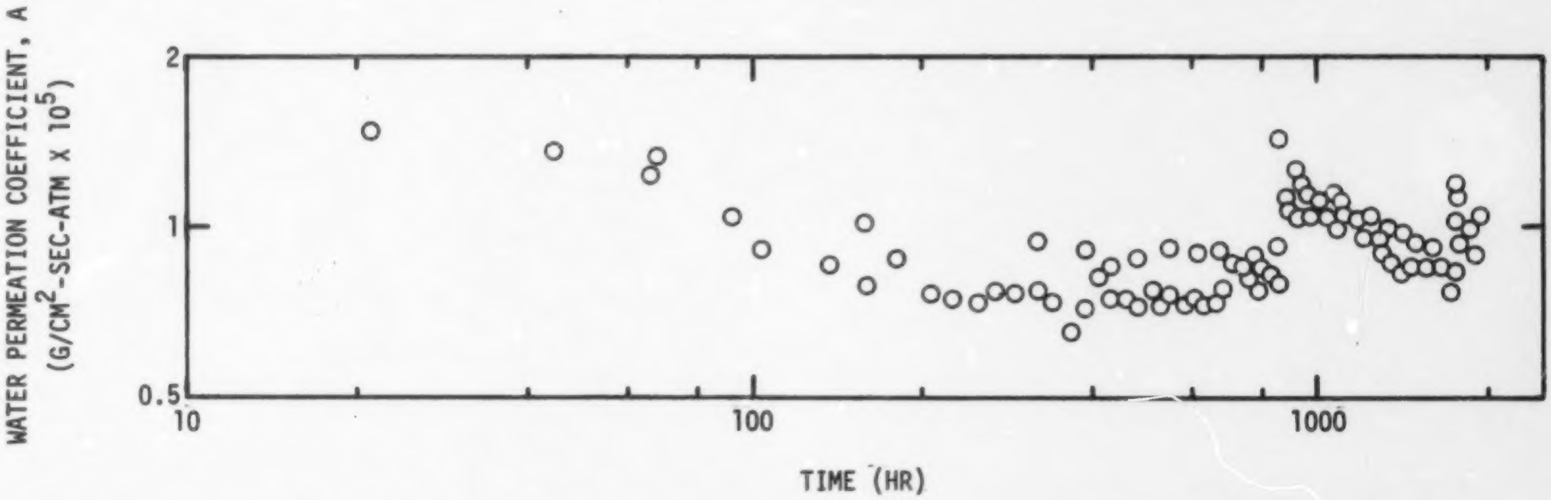


Fig. 22. Unit II: secondary effluent water permeation coefficient versus time - Experiment II

graphs, the greatest flux decline occurred during the initial 100 hr. After that significant flux decline, the permeate water production was maintained with periodic cleanings. It appears from the data that both cleaners (EDTA and the sodium perborate) performed equally throughout the experiment. In agreement with the first experiment, BIZ enzyme detergent also did a good job of flux restoration. Because there has been little difference in the ability of EDTA, BIZ, and sodium perborate to clean the reverse osmosis units, it is recommended that the least expensive, sodium perborate, be used whenever possible.

Figure 23 is a graph of the salt rejection behavior, as based on conductivity measurements, for Units I and II. Both units maintained approximately a 96% salt rejection throughout the duration of the second experiment. It should be noted, however, that Unit I did experience a drop in rejection because of a faulty O-ring on one of the modules. This O-ring was replaced, and the rejection returned to a high level. Reductions of the more important substances associated with pollution were shown in Table 8, along with the Experiment I data. Chemical oxygen demand and phosphate rejections were excellent, and ammonia nitrogen rejections were very good.

Typical results of characterization measurements made during the second experiment are given in Table 9. These data and those obtained in other measurements taken during Experiment II were quite similar to the Experiment I data on secondary effluent. Of particular interest was the high aromatic hydroxyl content of the feed stream. The particle size of this fraction was less than 0.45 μ for this set of data.

Another set of data taken November 25, 1970 (see Table 10) indicates that a significant portion of the aromatic hydroxyl material was greater than 8 μ in diameter in the sand-filtered treated feed. This was attributed to the poor performance of the sand filters, which were swimming-pool filters having only a 10-in. bed depth. Sand filters having a 30-in. bed depth were substituted in subsequent experiments.

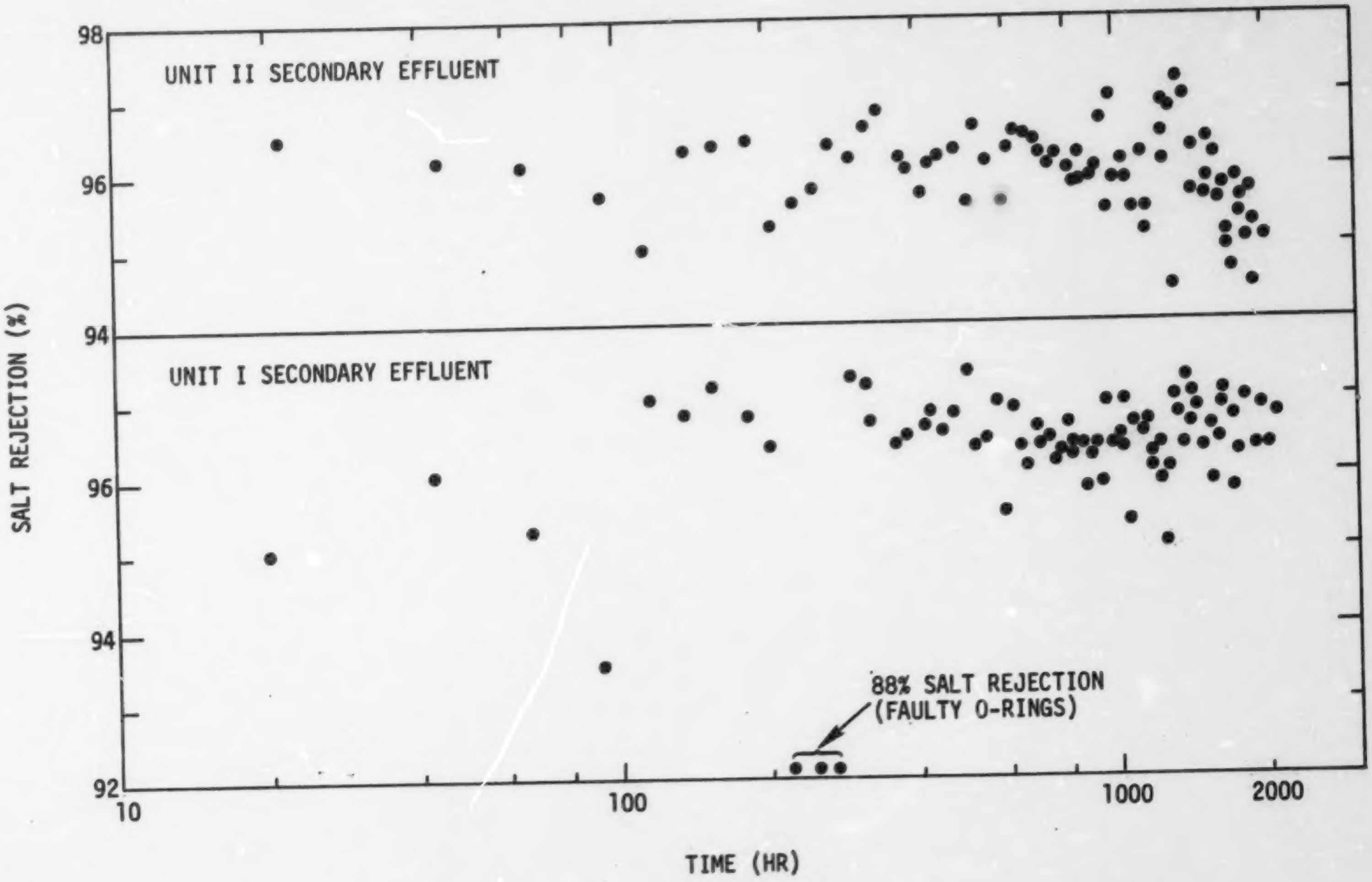


Fig. 23. Units I and II: salt rejection versus time - Experiment II

TABLE 9
STREAM CHARACTERIZATION DATA, OCTOBER 28, 1970 - EXPERIMENT II

Stream Sampled	pH	Turbidity (JTU)	TOC, Unfiltered (mg/l)	UV Absorb. at 275 mμ	Aromatic Hydroxyl Content as Humic Acid (mg/l)	
					Unfiltered	Filtered, 0.45 μ
Unit I						
Secondary effluent	6.6	2.3	8	0.112	10	10
After acid and chlorine addition	3.8	1.8	10	0.127	10	10
Permeate	4.5	0.04	0	0.006		
Concentrate	3.5	2.0	16	0.206	17	16
Unit II						
Secondary effluent	6.7	2.2	6	0.104		
After acid and chlorine addition	5.5	2.5	9	0.120		
Permeate	4.9	0.05	0	0.007		
Concentrate	5.1	1.7	16	0.214		

TABLE 10
STREAM CHARACTERIZATION DATA, NOVEMBER 25, 1970

Stream Sampled	Filtered Fraction	UV Absorb. at 275 mμ	TOC (mg/l)	Aromatic Hydroxyl Content as Humic Acid (mg/l)
Secondary effluent		0.141	11	26.1
	8 μ	0.107	9	24.9
	1.2 μ	0.110	8	25.0
After chemical addition and sand filtration		0.156	14	22.9
	8 μ	0.128	13	21.4
	1.2 μ	0.120	12	21.2

Membrane deposit analysis results were reported in Section IV.

In comparing the first two experiments, it was noted that the product water flux declined at a much greater rate in the second experiment than in the first with the same feed used. Both experiments employed the same initial recovery and product water flux. However, in Experiment II the membrane permeability was lower and a higher pressure (550 versus 320 psi) was needed to achieve the same initial product water flux. If fouling were solely dependent on the quantity of water produced, one would expect similar flux decline rates. However, the higher pressure appears to cause a greater flux decline--much greater than can be explained by membrane compaction alone.

Another difference between the two experiments was the cleaning agents employed. The enzyme presoak BIZ was used exclusively in the first run. Since the cleaning agents and the pressure were both changed in the second run, one could argue that either or both were responsible for the greater flux decline. For that reason, both units were cleaned with BIZ several times during the run. The data indicated that there was no significant difference between the cleaning ability of the three cleaners.

Experiment IV - Constant Permeate Flow

The purpose of the fourth experiment was to more closely simulate actual plant operation by running at a constant product flux of 10 gfd. To achieve this product flux level, feed pressure was allowed to vary up to a limit of 600 psig (although in one instance this level was exceeded). Cleaning frequency was based upon the level and rate of change of feed pressure.

Unit I was employed for this experiment, and the process flow diagram is shown in Fig. 6. The unit was loaded with an improved version of the Model 4000 spiral-wound module. The modules each had 60 ft^2 of high-flux membrane cast on D-601 sailcloth backing, 0.045 in. polypropylene Vexar brine spacers, and melamine-treated tricot product water channels. Cleaning procedures were the same as described for Experiment II. Sodium perborate, EDTA, and BIZ were all used to clean the membrane surface.

Initially, a pressure of 435 psi was required to obtain an actual product flux of 10 gfd. The flux, normalized to 77°F, was 11.6 gfd. This corresponded to a water permeation coefficient of 1.93×10^{-5} g/cm^2-sec-atm.

Figures 24 and 25 indicate the time behavior of feed pressure and water permeation coefficient throughout the first 2800 hr of the run. To obtain longer-term operation data, the experiment was continued beyond the contract period. Because of membrane fouling, the pressure required to maintain a constant product flux rose but could be partially recovered by cleaning. After approximately 800 hr with little change in pressure, a large increase in feed pressure was required to maintain the 10 gfd permeate flow. Changing cleaners did not arrest the permeation coefficient decline. At 1430 hr, the unit was shut down, cleaned with BIZ, and fed with tap water for 72 hr. This resulted in a flux increase of greater than 100%. A higher membrane coefficient and lower feed pressure were maintained with bi-weekly BIZ cleanings for another 800 hr. Then the required feed pressure rose again. It was reduced to the 425- to 525-psig range again by relaxing the permeate flow requirement to 8.5 to 9.0 gfd.

Since completion of the contract, feed pressure rise has been better controlled by using heated cleaning solutions (140°F). Feed pressures of less than 500 psig have been required to maintain a permeate flux of 10 gfd.

Figure 26 is a logarithmic plot of water permeation coefficient versus time. The slope is -0.0517, which compares favorably with the results of the first experiment, when the greater pressure and permeate flux are taken into account.

Figure 27 shows that the salt rejection, determined by conductivity measurements during the constant permeate flow test, remained high throughout the test period and appeared to decrease slightly below the initial value. In

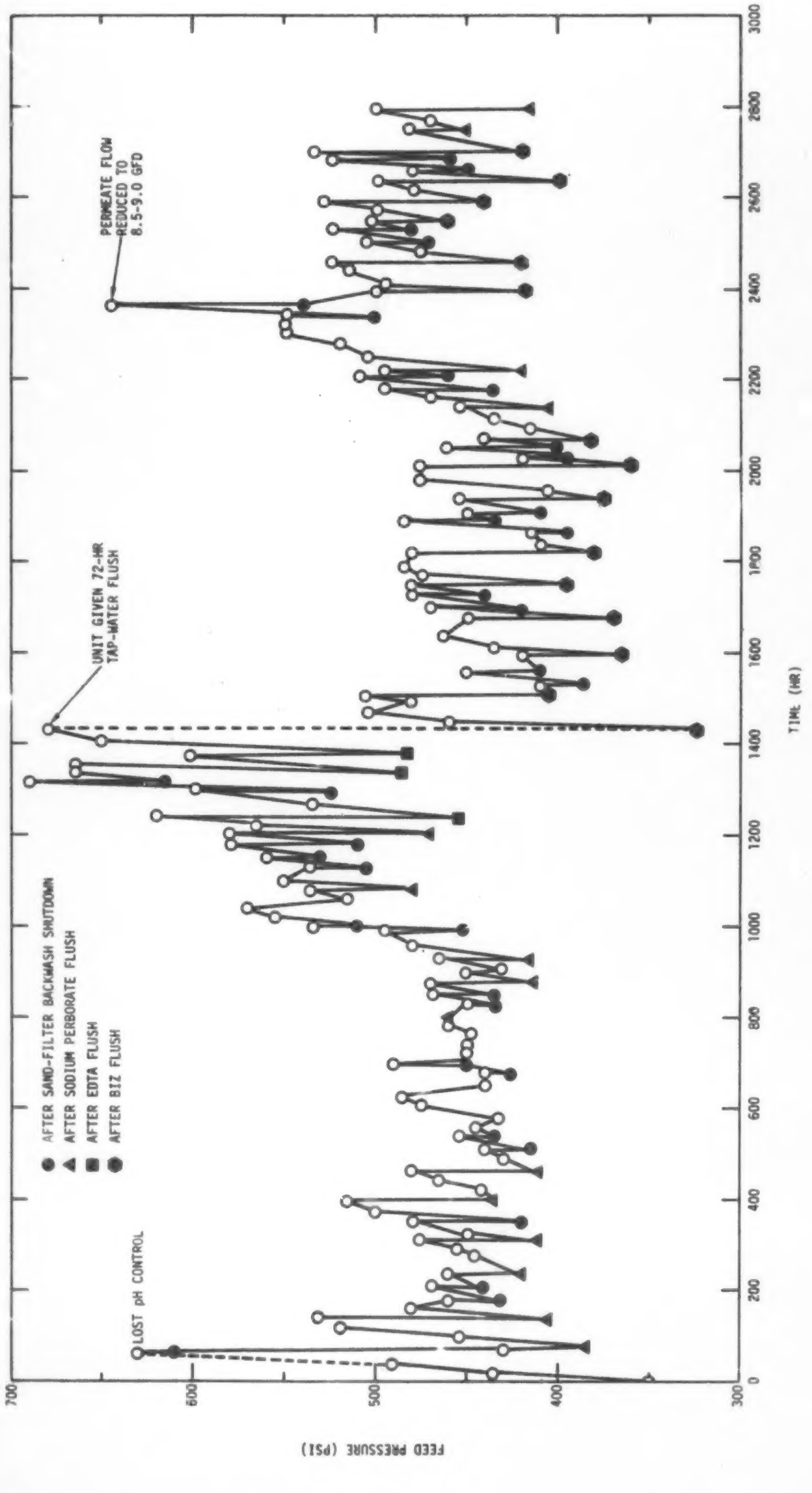


Fig. 24. Experiment IV: feed pressure versus time

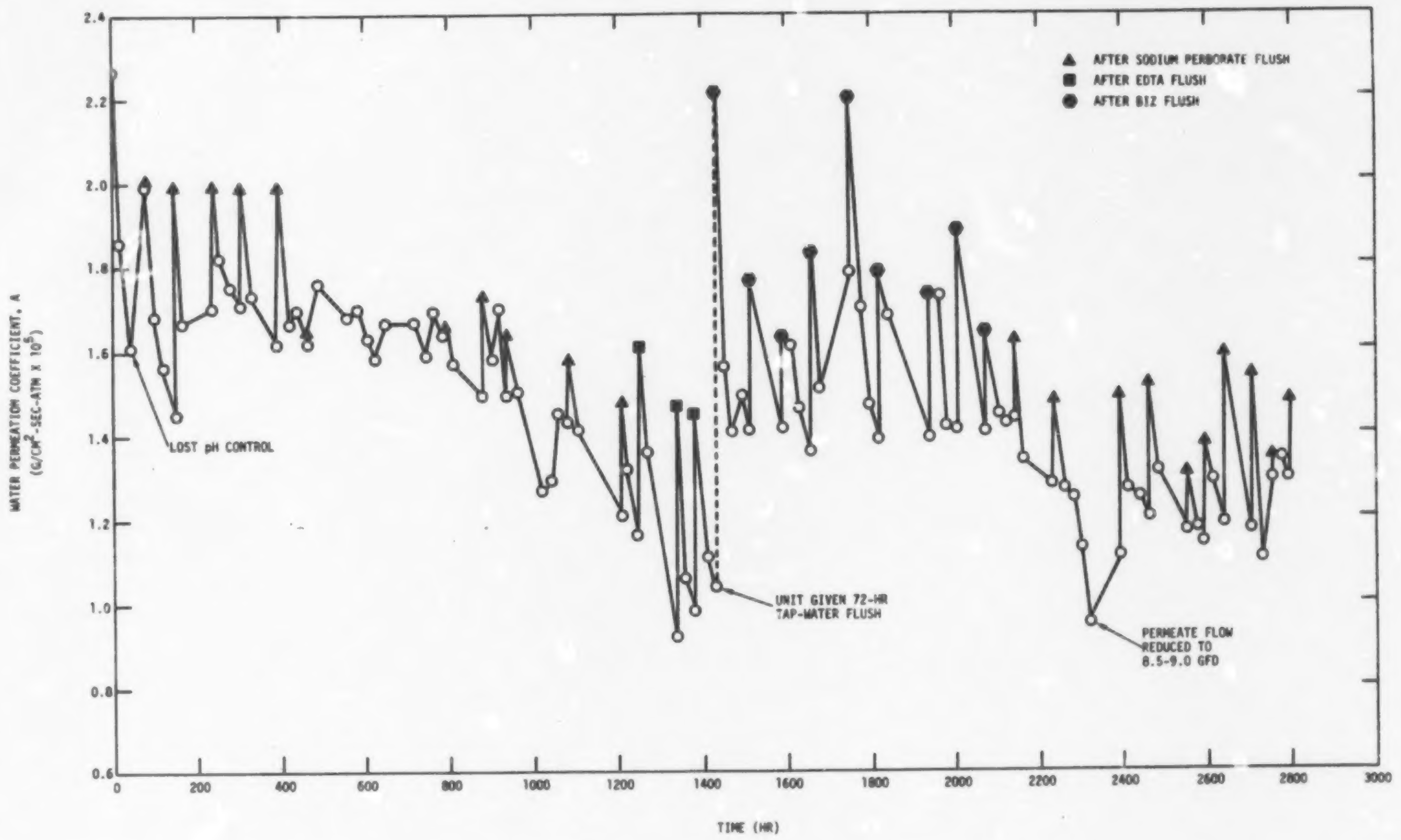


Fig. 25. Experiment IV: water permeation coefficient versus time

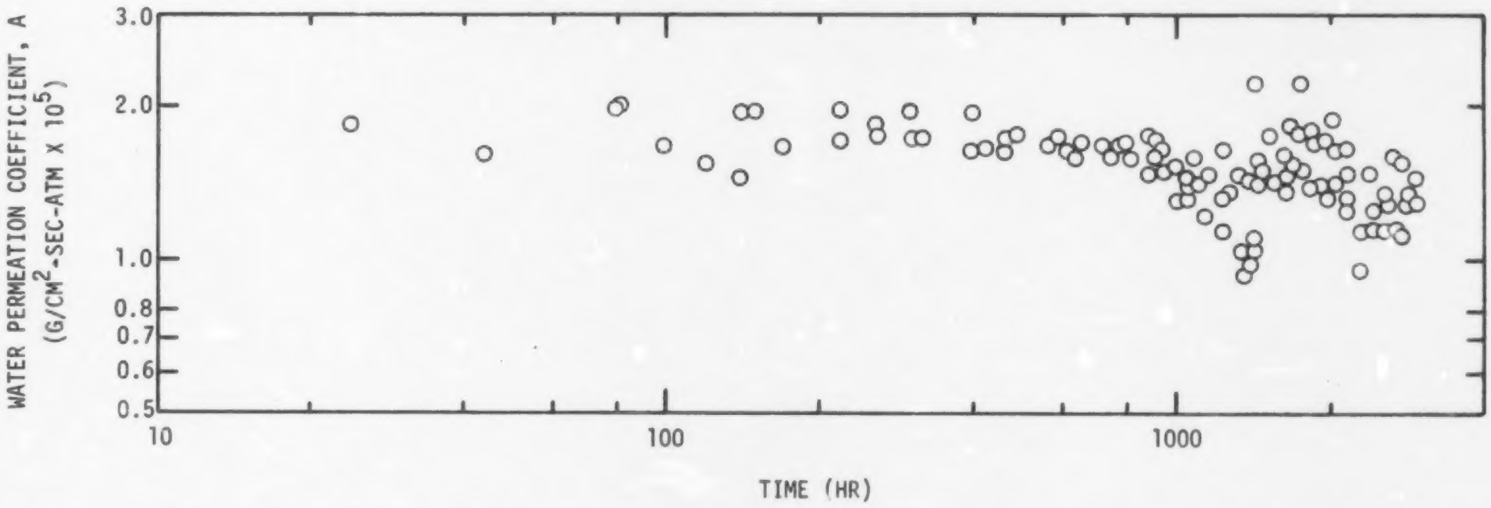


Fig. 26. Experiment IV: logarithmic plot of water permeation coefficient versus time

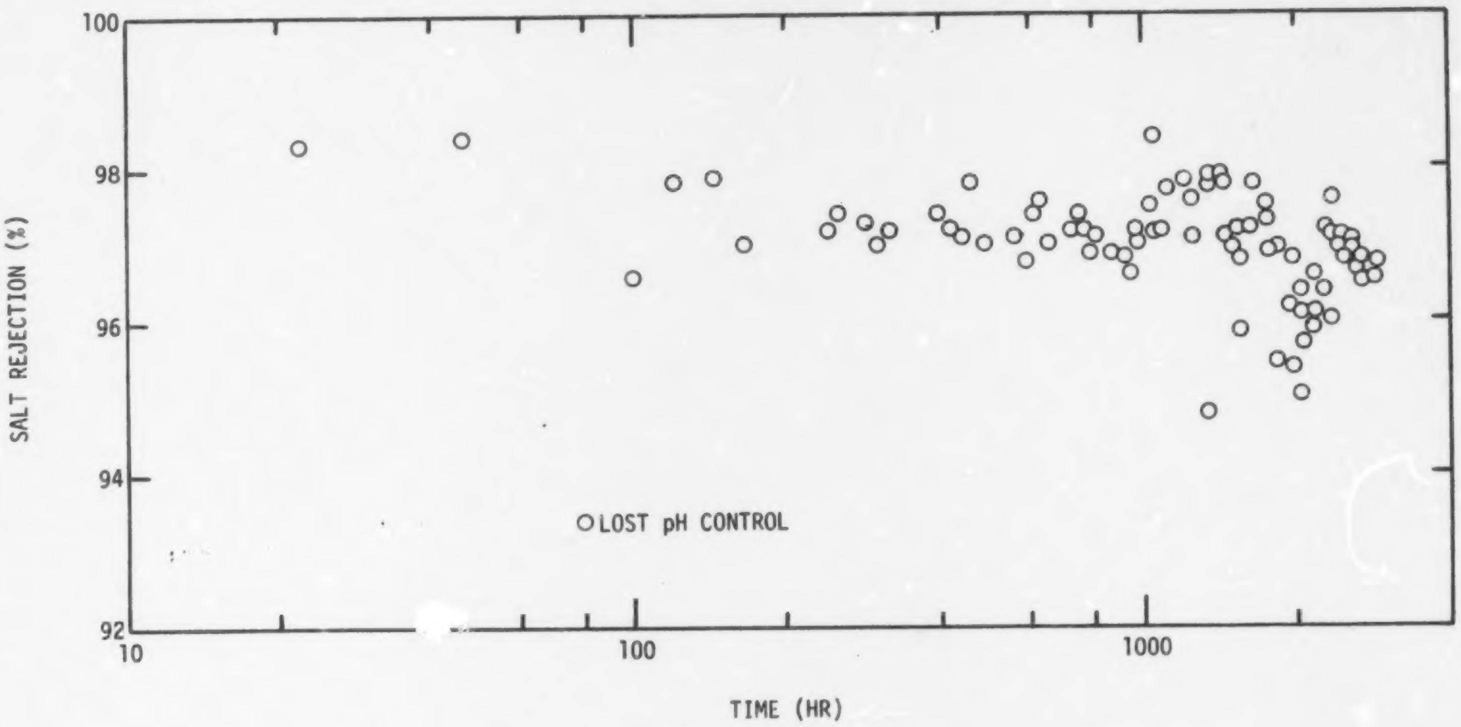


Fig. 27. Experiment IV: salt rejection versus time

most of the other experiments, salt rejection increased slightly above the initial value. Percent reductions of substances associated with pollution were similar to those given in Table 8.

A membrane deposit analysis of a module removed from the unit after the contract period was described in Section IV.

In conclusion, Experiment IV demonstrated the ability to operate a reverse osmosis unit on sand-filtered activated-sludge effluent with minimal pretreatment. Permeate fluxes of 8 to 10 gfd were maintained by adjustments in feed pressure and cleaning frequency. These encouraging results should be tested on a larger unit to obtain detailed operational cost data.

REVERSE OSMOSIS UNIT OPERATION ON PRIMARY EFFLUENT

Experiments were carried out on primary effluent using both the field test and trailer mounted experimental units with several levels of pretreatment. Exploratory tests were conducted with no pretreatment and with sand filtration only. More extensive testing was carried out with chemical clarification plus sand filtration and chemical clarification plus sand filtration plus carbon adsorption as pretreatment. A physicochemical treatment facility was designed and constructed adjacent to the primary clarifier at the Pomona plant. It was operated over eight months to provide feedwater to the pilot plant reverse osmosis units. Appendix B gives typical results.

Primary Effluent Tests with Minimal Pretreatment

Some exploratory tests were conducted using primary effluent with either no pretreatment or sand filtration as a reverse osmosis unit feed. The trailer-mounted experimental unit was used for the tests with sand filtration. A Gulf Environmental Systems owned unit especially designed for feedwaters containing large amounts of suspended solids was used for the experiments with no pretreatment.

With the trailer-mounted experimental reverse osmosis unit, successful operation for more than 100 continuous hours was not attained. A significant factor was that the sand filter with this unit did a poor job of removing suspended matter, which resulted in brine channel plugging. The filter was designed for swimming-pool operation and had only a 10-in. bed depth. Even with frequent backwashing, the surface layer of sand became plugged with suspended matter and channeling developed within the filter.

The other feasibility experiment on primary effluent was carried out using a reverse osmosis unit owned by Gulf Environmental Systems. This unit was designed for operation on waters containing significant amounts of suspended solids. It contained six 10-ft pressure vessels, each of which contained four modules. Modules used in this experiment had corrugated cellulose acetate sheet brine spacers, which provided a less tortuous flow path and hence less chance of plugging. Modules in the first four tubes each contained 30 ft^2 of membrane. The fifth tube contained 20-ft^2 modules, and the sixth contained 15-ft^2 modules. There were 620 ft^2 of membrane in the unit. The unit also had provisions for automatic depressurization. During the tests, programmed depressurization was set on a 2-hr cycle: 110 min on, 7-min pause, and 3-min backflush.

Table 11 shows the results of a chemical analysis performed by the Los Angeles County Sanitation District on the feed, brine, and product streams on June 24, 1971. The permeate flux was initially 11 gfd. It dropped to 3 gfd within 200 hr and could be restored to 7 gfd by weekly BIZ cleanings. Modules in tubes 5 and 6, which operated at brine velocities approximately 1.5 and 2 times those in the first tubes, showed less flux decline. This preliminary experiment indicated that operating on primary effluent with spiral modules is feasible. Programmed depressurization appeared to reduce the cleaning frequency. Optimization experiments have been proposed for a continuation program.

TABLE 11
CHEMICAL ANALYSIS FOR PRIMARY EFFLUENT

	Concentration (mg/1)			Percent Reduction[a]
	Blended Feed	Permeate	Concentrate	
Sodium	276	10	300	96.5
Potassium	30	1.1	31.2	96.5
Ammonia nitrogen	51.5	2.5	54.8	95.2
Calcium	152	1.5	168	99.6
Magnesium	37	<0.1	38.6	>99.6
Chloride	275	11	290	96
Nitrate nitrogen	0.76	0	0.76	--
Sulfate	514	1	572	99.9
Orthophosphate	16.1	<0.18	16.8	>99.9
Total COD	318	16.6	336	94.7
Dissolved COD	145	14.5	139	90.1
Total alkalinity	166	28	178	--
Turbidity (JTU)	116.8	0.08	123.2	∿100
pH (pH units)	6.7	6.3	7.8	--
TDS	1548	32	1593	98.2
Conductivity (μmho)	2380	98	2430	96.0

[a] Based on feed concentration.

Experiment III - Chemically Clarified Primary Effluent With and Without Activated-Carbon Pretreatment

The purpose of the third experiment was to determine reverse osmosis operating behavior on primary effluent that had received additional physical and chemical clarification. Figures 1 and 6 show the flow diagram for this test. Effluent from the Pomona plant primary clarifier was chemically coagulated and fed to a sludge blanket clarifier. Ferric chloride was used as a coagulant along with a polyacrylamide coagulant aid, Magnifloc 905-N (American Cyanamid). Overflow from the clarifier divided and passed through pressurized sand filters. One stream then flowed to Unit II with the same pretreatment scheme as used in Experiments I and II. The other stream flowed through a downflow activated-carbon adsorber. It then passed through the Unit I pretreatment sequence. The cleaning sequence was the same as described for Experiment II. Sodium perborate was initially selected as the cleaner.

In this experiment both units were loaded with new Model 4000 spiral-wound modules. The operating conditions consisted of a pressure of 400 psig and 75% to 80% water recovery. Unit I (carbon-treated effluent) initially (19 hr) produced 15.8 gfd with a water permeation coefficient of 2.9×10^{-5} g/cm^2-atm-sec and a conductivity rejection of 91.5%. Unit II (sand-filtered effluent) initially (19 hr) produced 15.1 gfd with a water permeation coefficient of 2.5×10^{-5} g/cm^2-atm-sec and a conductivity rejection of 95%.

Figures 28 and 29 indicate the permeate flux, normalized to 77°F, of the two units versus time. The permeate flux declined to 9 to 11 gfd in both units during the first 200 hr. To determine the nature of the membrane fouling deposits, a module was removed from Unit I. Analysis revealed the presence of significant quantities of iron (see Section IV), which presumably carried over in colloidal form from the clarifier. EDTA was then employed as a cleaner and did a good job of maintaining the flux. The cleaning frequency was also increased to three days a week in Unit II because of the heavier organic content of the feed.

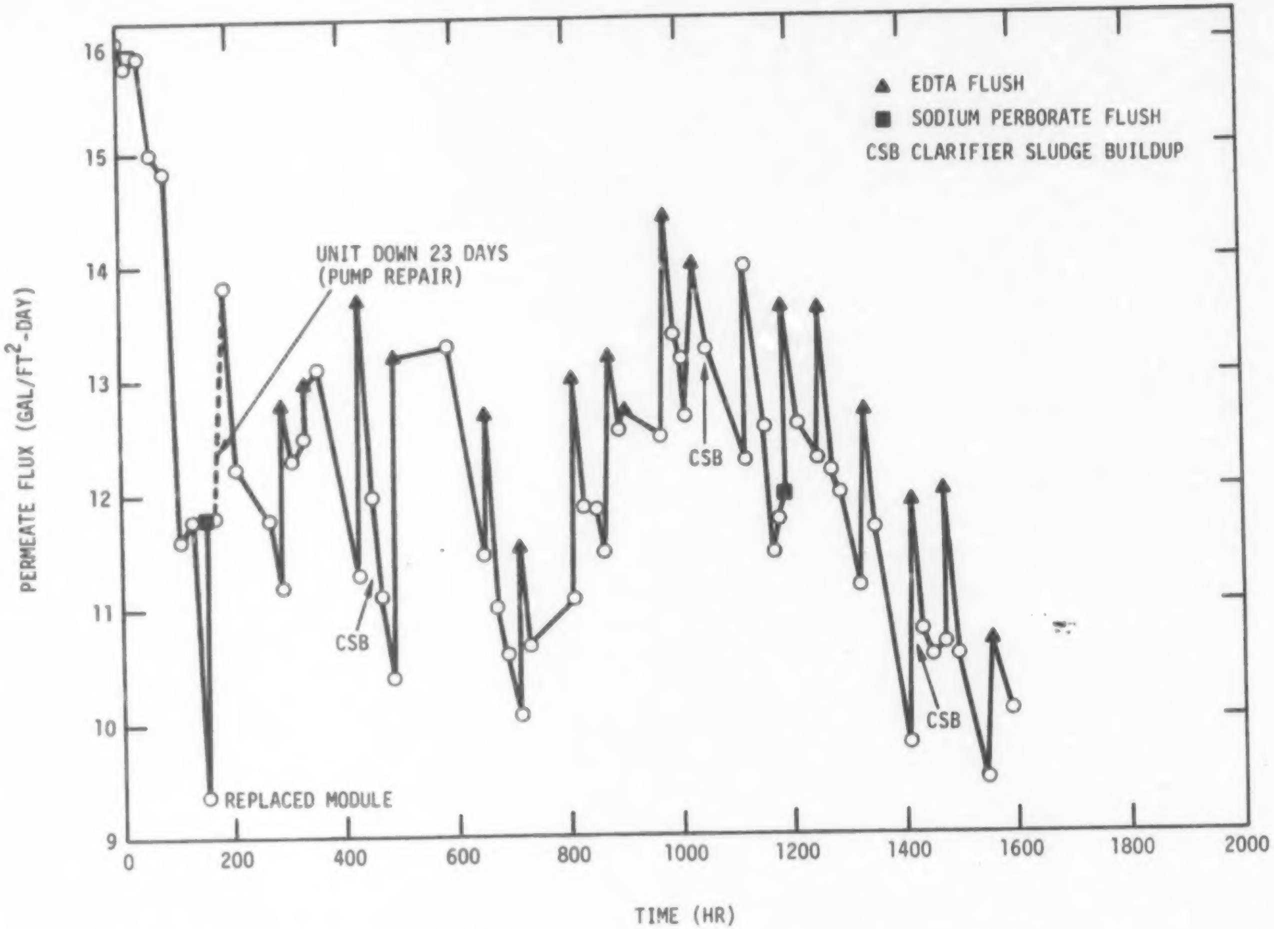


Fig. 28. Carbon-treated chemically clarified primary effluent: permeate flux versus time - Experiment III

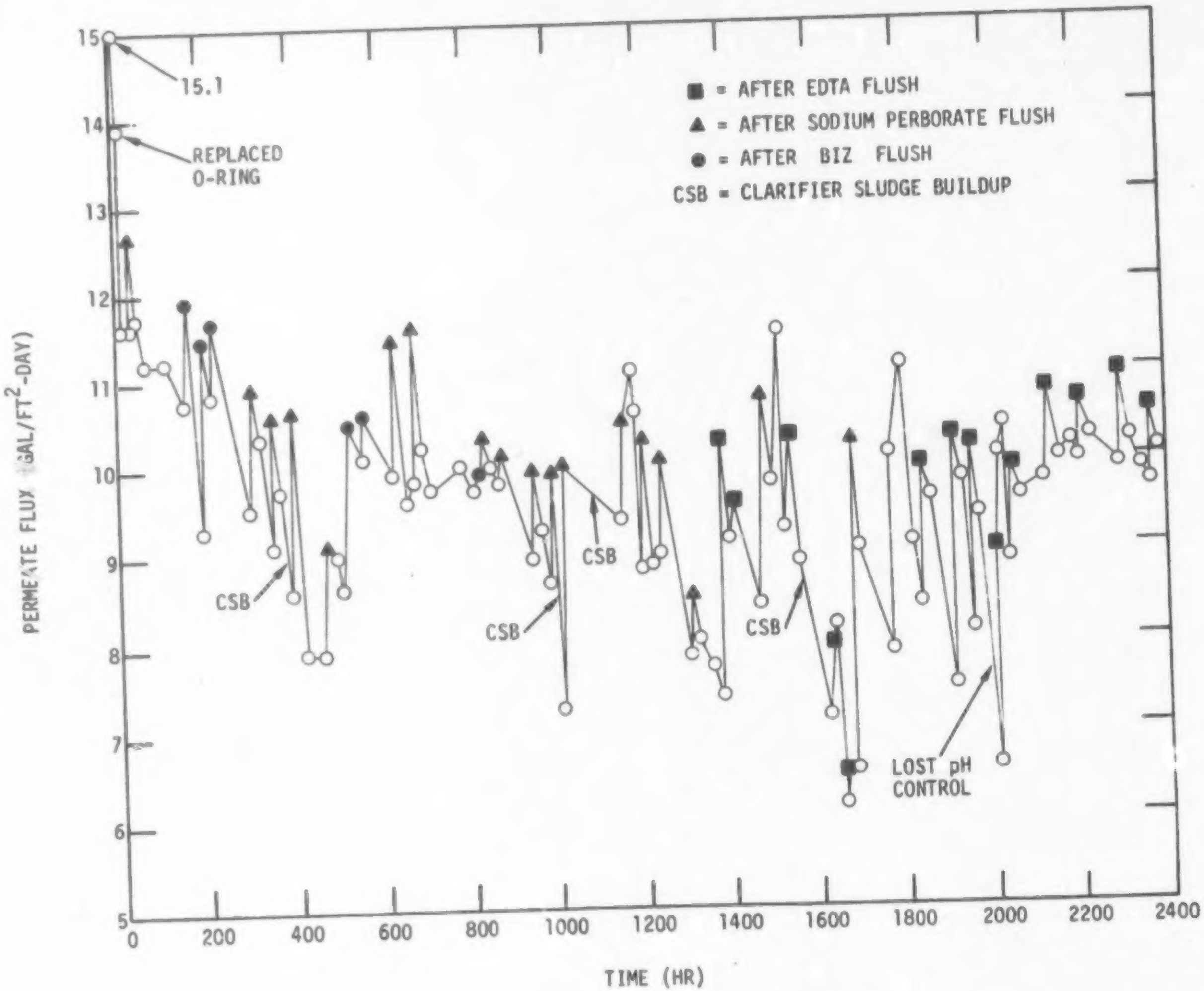


Fig. 29. Sand-filtered chemically clarified primary effluent: permeate flux versus time - Experiment III

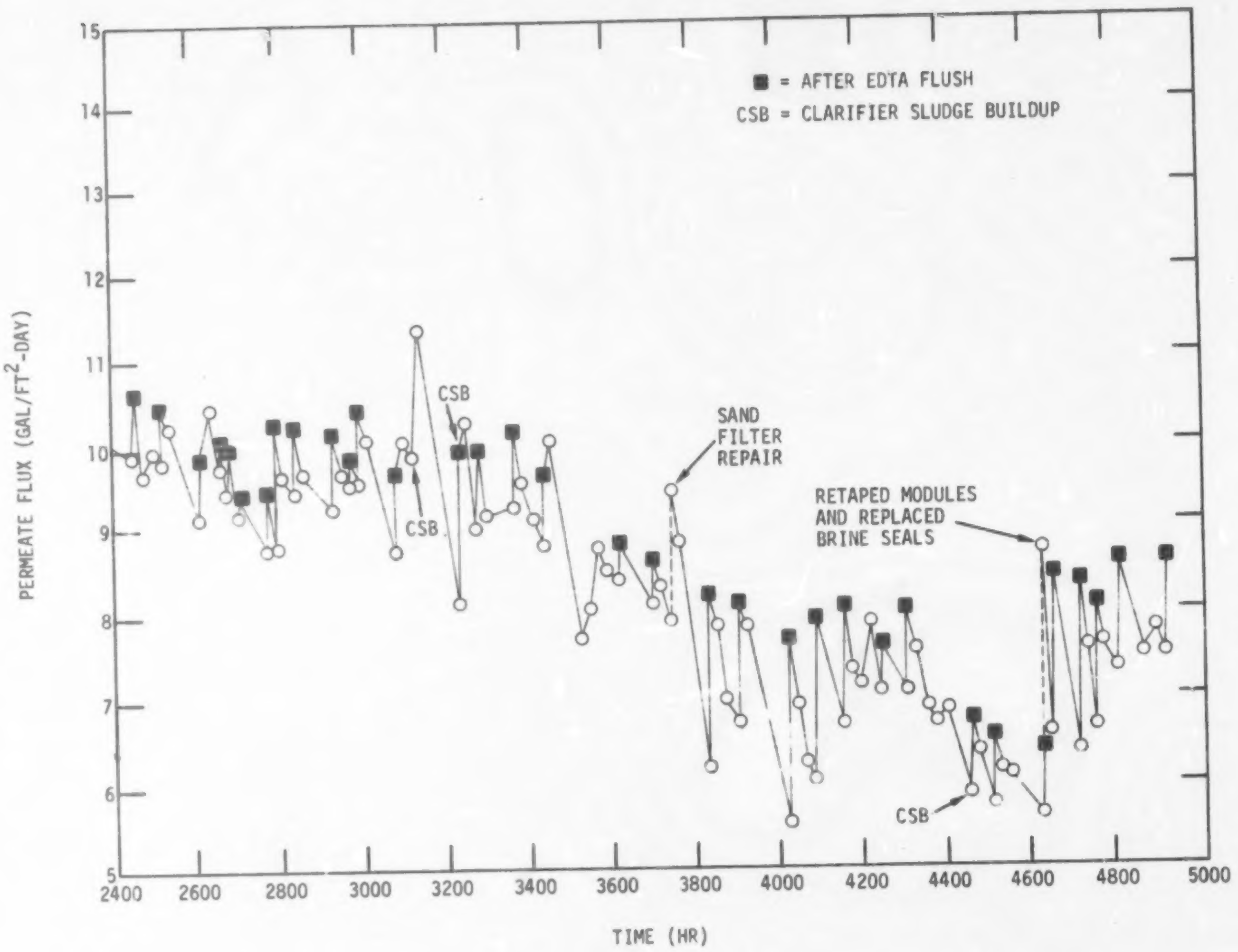


Fig. 29. (Continued)

It was difficult to keep a constant feed quality to the units because of periodic sludge buildup and carryover from the clarifier. These occurrences are noted in Figs. 28 and 29. In many cases, permeate flux in the units dropped off at roughly the same time as the sludge buildup was noted.

Flux restoration caused by depressurization and a long period of chlorinated-tap-water flushing was again demonstrated when the pump on Unit I failed and the unit was down for 23 days. The gain in performance was short-lived. However, this technique does appear to have some promise in restoring flux in units that have been improperly operated or have been subjected to a feed upset.

The test on carbon effluent was deliberately discontinued after 1588 hr. It was evident at that time that the carbon column was unnecessary. Although Unit II required more frequent cleaning than Unit I, the added cost was much less than activated-carbon pretreatment. To determine the flux behavior over a longer time span, the Unit II test was continued one month beyond the end of the contract period. At about 4200 hr, fluctuations in sludge carry-over from the clarifier caused a buildup of organics in the modules. This, in turn, damaged the module outer wrap tapes and several brine seals were "blown." Repair of the tape and seals at about 4600 hr yielded a significant flux improvement, but it was evident that permanent damage had occurred. The test was terminated at 4940 hr.

Figures 30 and 31 indicate the log-log variation in membrane coefficient with time. The flux decline slope was -0.049 for Unit I and -0.074 for Unit II. These are approximately twice the slopes achieved in Experiment I on activated-sludge effluent (-0.025 and -0.037 for carbon-treated and sand-filtered, respectively).

Salt rejections of both units versus time are plotted in Fig. 32. Unit I, which had a higher flux membrane, had an initial salt rejection of 91.5%. Unit II had an initial salt rejection of 96% (20 hr). Rejection in Unit I decreased slightly over the run. On the other hand, salt rejection in

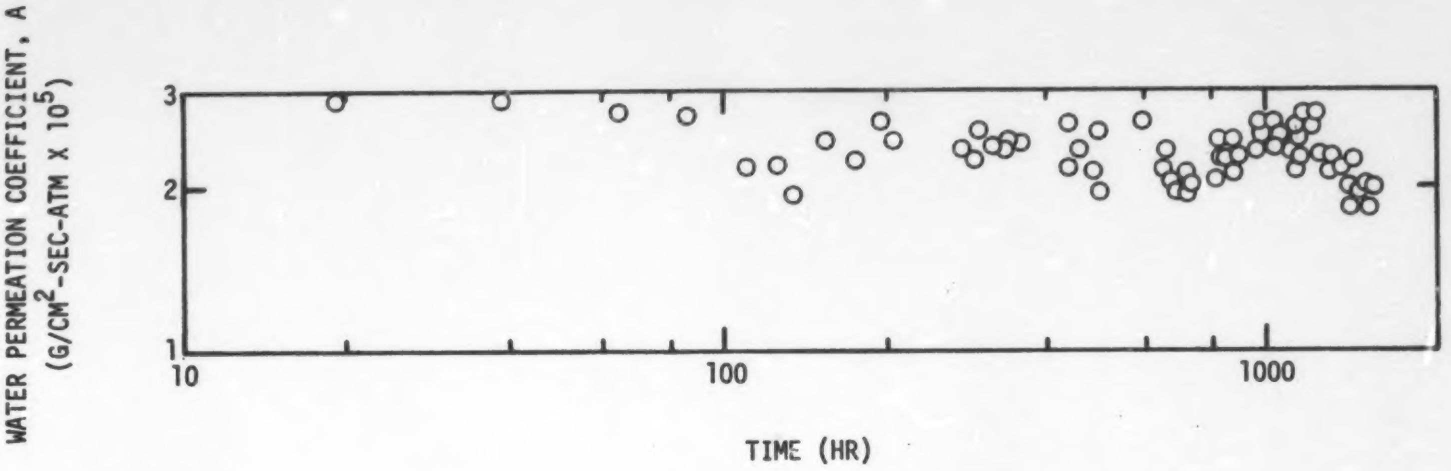


Fig. 30. Carbon-treated chemically clarified primary effluent: water permeation coefficient versus time - Experiment III

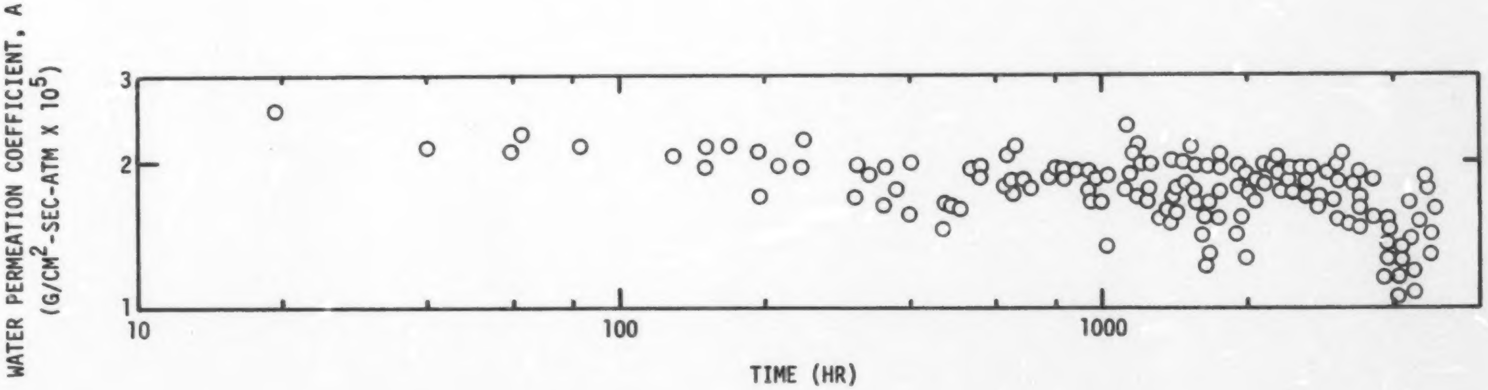


Fig. 31. Chemically clarified primary effluent: water permeation coefficient versus time - Experiment III

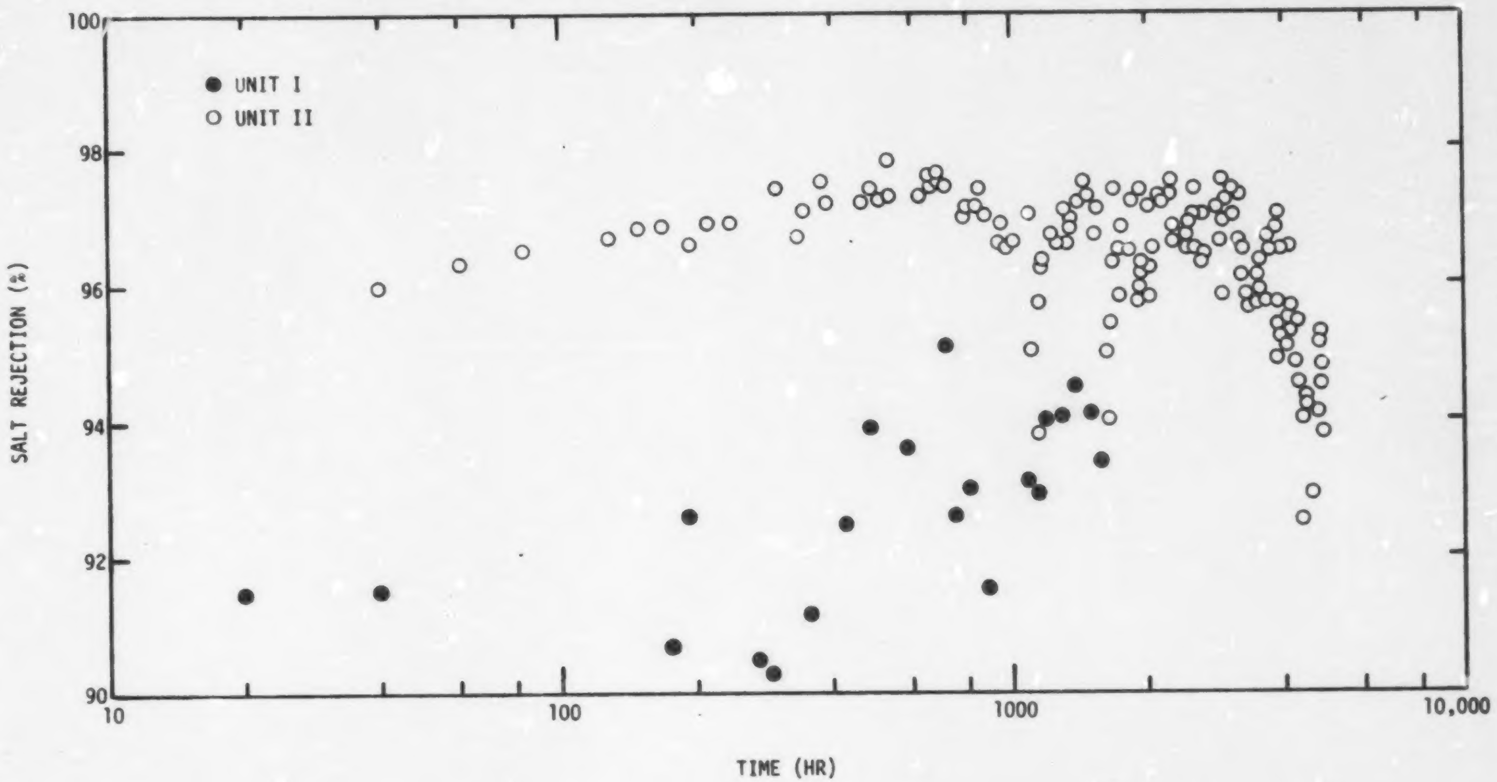


Fig. 32. Unit I and II salt rejection versus time - Experiment III

Unit II increased to about 97% until 4200 hr, when it was decreased by "blown" brine seals and partial module plugging by excessive clarifier sludge carryover.

Reductions of individual feed solutes are presented in Table 12. With the exception of COD, solute reductions were similar to the activated-sludge effluent data. Product COD concentrations with primary effluent were very similar with all three pretreatment levels: sand filtration, chemical clarification and sand filtration, and chemical clarification followed by activated-carbon pretreatment. This indicated that the organic compounds that permeated the membrane survived physicochemical treatment. However, they appeared to be destroyed or significantly reduced by biological treatment, as evidenced by the very small amounts of organic matter in the permeate in the secondary effluent tests.

Samples of the permeates with all levels of pretreatments were analyzed for low-molecular-weight compounds that were known to be poorly rejected. Low-molecular weight acid and organic nitrogen compounds were not present at significant levels. The exact nature of the compounds in the permeate was not determined. However, it was discovered in the laboratory studies that most of the organic carbon in the permeate could be removed by air purging.

Short air purges removed an average of 80% of the TOC in the permeate from Unit I and an average of 60% of the TOC in the Unit II and experimental unit permeates. The remainder could be almost completely removed by passage through activated carbon (Calgon Filtersorb 400). It was concluded that the primary effluent permeates contained two principal fractions:

1. A volatile fraction, not UV-sensitive, incompletely removed by carbon, which can be removed by purging with air.

2. A nonvolatile fraction containing UV-sensitive material which can be removed by carbon and Dowex-11. This fraction also contains non-UV-sensitive material which is removable only by carbon.

TABLE 12
REDUCTION OF FEED SOLUTES, CHEMICALLY CLARIFIED PRIMARY EFFLUENT

	Feed[a] Concentration (mg/l)		Product Concentration (mg/l)		Percent Reduction[b]
	Average Value	Range	Average Value	Range	
Calcium	91	54-114	0.4	<0.1-1.2	>99.6
Magnesium	19.8	13.3-26	0.13	<0.1-0.3	>99.3
Sodium	133	92-188	10	6.3-17	92.5
Potassium	21.3	17.2-29	1.8	0.7-2.6	91.5
Ammonia-N	46.8	37.5-57	4.6	2.8-7.5	90.2
Chloride	277	209-378	26.6	14-44	90.4
Sulfate	325	256-388	0.7	Nil-3	>99.8
Phosphate	1.7	0.27-3.1	0.01	<0.1-0.08	>99.4
Total COD	70	24-109	24	15.7-33.4	65.7
Dissolved COD	64	22.2-103	22	15.7-32.3	65.6
TDS	963	757-1170	65	49-92	93.3

[a] Feed contained recycled brine.

[b] Based on feed concentration.

Typical characterization data are listed in Table 13. These results show that a substantial proportion of the TOC and hydroxyaromatic material is greater than 8 μ. The hydroxyaromatic content of the primary effluent feed stream is high, even after pretreatment. However, no evidence of hydroxyaromatic material could be found in the permeate.

In conclusion, Experiment III demonstrated that reverse osmosis operation on chemically clarified primary effluent was quite promising. As in the secondary effluent tests, activated-carbon pretreatment was shown to be unnecessary. It is recommended that additional long-term tests be conducted under more uniform clarifier operation with aeration of the permeate stream.

CORRELATION OF PERMEABILITY DECLINE WITH FEEDWATER PROPERTIES

The four field tests indicated that reverse osmosis unit operation on primary and secondary effluents with minimal additional pretreatment is technically feasible. Activated-carbon pretreatment was shown to be unnecessary for sustained operation. Product water flux could be maintained at a level close to 10 gfd by regular cleaning with either sodium perborate, EDTA, or BIZ enzyme detergent.

In all the runs, some of the membrane water permeability could not be recovered by cleaning. This permanent decline could represent either a pressure increase or a water flux decrease, depending on whether the unit was being operated at constant flux or constant pressure. For all runs except Experiment II, data on permanent permeability decline with time could be represented by straight-line log-log plots. Slopes of the lines are summarized below:

Experiment	Feed Stream	Slope of Log-Log Permeation Coefficient Decline Plot
I	Carbon-treated secondary effluent	-0.025
I	Secondary effluent	-0.037
IV	Secondary effluent	-0.0517

TABLE 13
STREAM CHARACTERIZATION DATA, JANUARY 26, 1971 - EXPERIMENT III

Stream Sampled	Fraction Passed Thru Membrane Filter	pH	Turbidity (JTU)	TOC (mg/1)	UV Absorb. at 275 mµ	Aromatic Hydroxyl Content as Humic Acid (mg/1)
Primary effluent	<8 µ	7.1	71	56		61.5
				25.5	0.258	42
Experimental Unit						
After chemical addition	--	6.2	58	45.5		62
	<8 µ			28.5	0.258	41
After sand filtration	--	6.5	51	39.5		38
	<8 µ			26.5	0.219	31
Unit II						
After clarifier	--	6.6	16	16		26.5
	<8 µ			13	0.218	20.5
After chemical addition and sand filtration	--	3.3	6.9	23		47
	<8 µ			22	0.234	45
Blended feed	--	4.1	8			57
	<8 µ				0.264	56
Permeate	--	4.2	0.05			
	<8 µ				0.024	
Concentrate	--	4.1	1.8			94
	<8 µ				0.383	94
Secondary effluent	--	6.5	7			15.6
	<8 µ				0.111	12.3

Experiment	Feed Stream	Slope of Log-Log Permeation Coefficient Decline Plot
III	Chemically clarified primary effluent	-0.074
III	Carbon-treated chemically clarified primary effluent	-0.049

In general, permeability declines were greater for operation on primary effluent than for secondary effluent feeds. Activated-carbon pretreatment flattened the slope in all cases.

Several of the characterization techniques showed promise in indicating the fouling tendency of a reverse osmosis unit feed stream. Aromatic hydroxyl content, UV absorbance, turbidity, and COD appeared to be good indications of the fouling tendency of municipal effluents. Of these techniques, significant amounts of field data were gathered only for turbidity and COD. Figures 33 and 34 show the effects of these parameters on permeation coefficient decline. Turbidity showed the best correlation, although throughout each run the feedwater turbidity varied widely (see Fig. 16).

More data are needed to clarify the effect of feedwater COD on membrane fouling. One might expect a different correlation with primary than with secondary effluent because of the different state of oxidation. Actually, since the aromatic hydroxyl content appears to be more related to fouling, as indicated by the membrane deposit analyses, UV absorbance at 275 mμ may be a more valuable correlating parameter. Total organic carbon, which does not depend upon the oxidation state, may also offer some promise. However, a reliable TOC device for field measurements has not been found.

Some caution should be used in generalizing about the results of Figs. 33 and 34. First, log-log flux decline slopes are empirical, and it is very dangerous to extrapolate them beyond the data limits. Second, these results were obtained only on effluents at Pomona and may not be generally applicable. Third, no general correlation of membrane fouling with turbidity has been found.

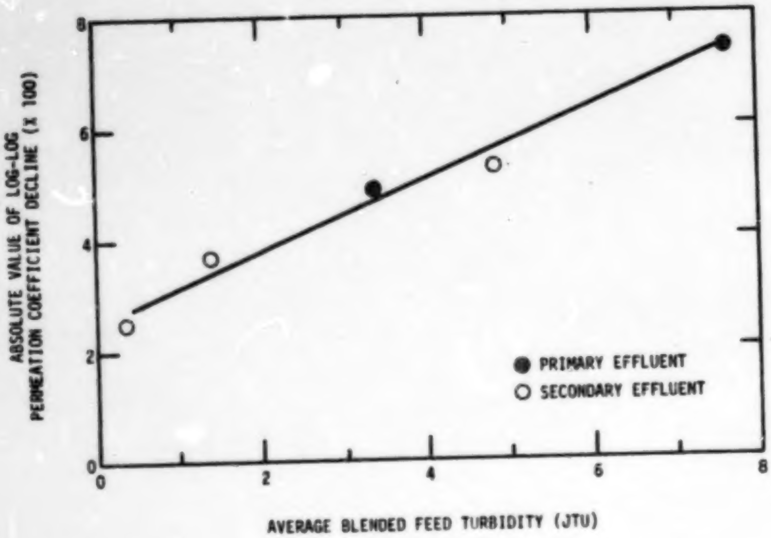


Fig. 33. Effect of feed turbidity on permeation coefficient decline slope

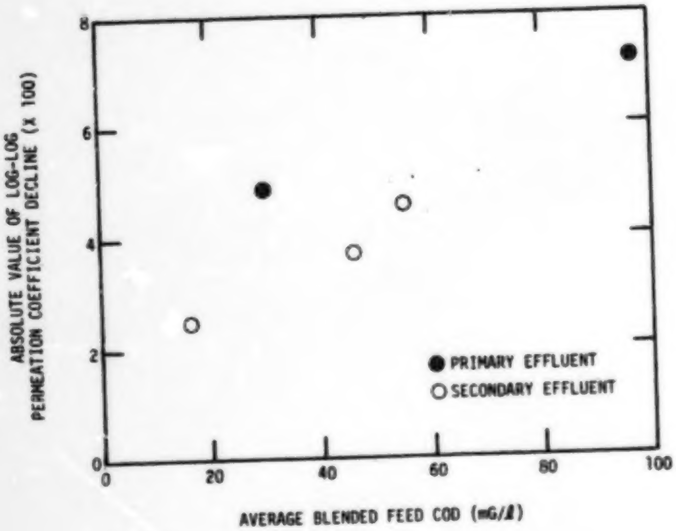


Fig. 34. Effect of COD on permeation coefficient decline slope

It is probably only a valid cause-and-effect relationship when the fouling deposits and the turbidity material compositions match.

SECTION VI

ECONOMICS OF REVERSE OSMOSIS TREATMENT OF SANITARY WASTEWATER

COST EFFECTIVENESS OF CLEANING

The four field experiments indicate that reverse osmosis units can be run at satisfactory levels of product water flux provided that cleanings are performed at regular intervals. Since the technical feasibility has been established, the important question now is whether or not the method is economical compared with extensive pretreatment. This section presents a simplified economic analysis of the methods. Costs are based on 1972 values.

Chemical Cleaning Cost

Three factors are considered in the cost of chemical cleaning: chemicals, operating labor, and increased initial and module replacement cost to make up for down-time. The costs of the chemicals used in the calculations are listed in Table 14.

Field cleaning results indicate that 0.025 gal. of solution for each square foot of membrane is required for one cleaning. The results also show that the cleaning interval should be based on the quantity of water produced. Figure 35 is a plot of the cost of the cleaning chemicals versus the cleaning interval expressed as gallons of permeate per square foot of membrane. Sodium perborate is the lowest-cost cleaner. Based on a permeate flux of 10 gfd and a 3.5-day cleaning cycle (a typical test condition), the perborate cost is 2.25¢/1000 gal. The cleaning cost is proportional to the reciprocal of the interval. Thus, at low intervals between cleanings (below 20 gal./ft^2), the cost becomes excessive.

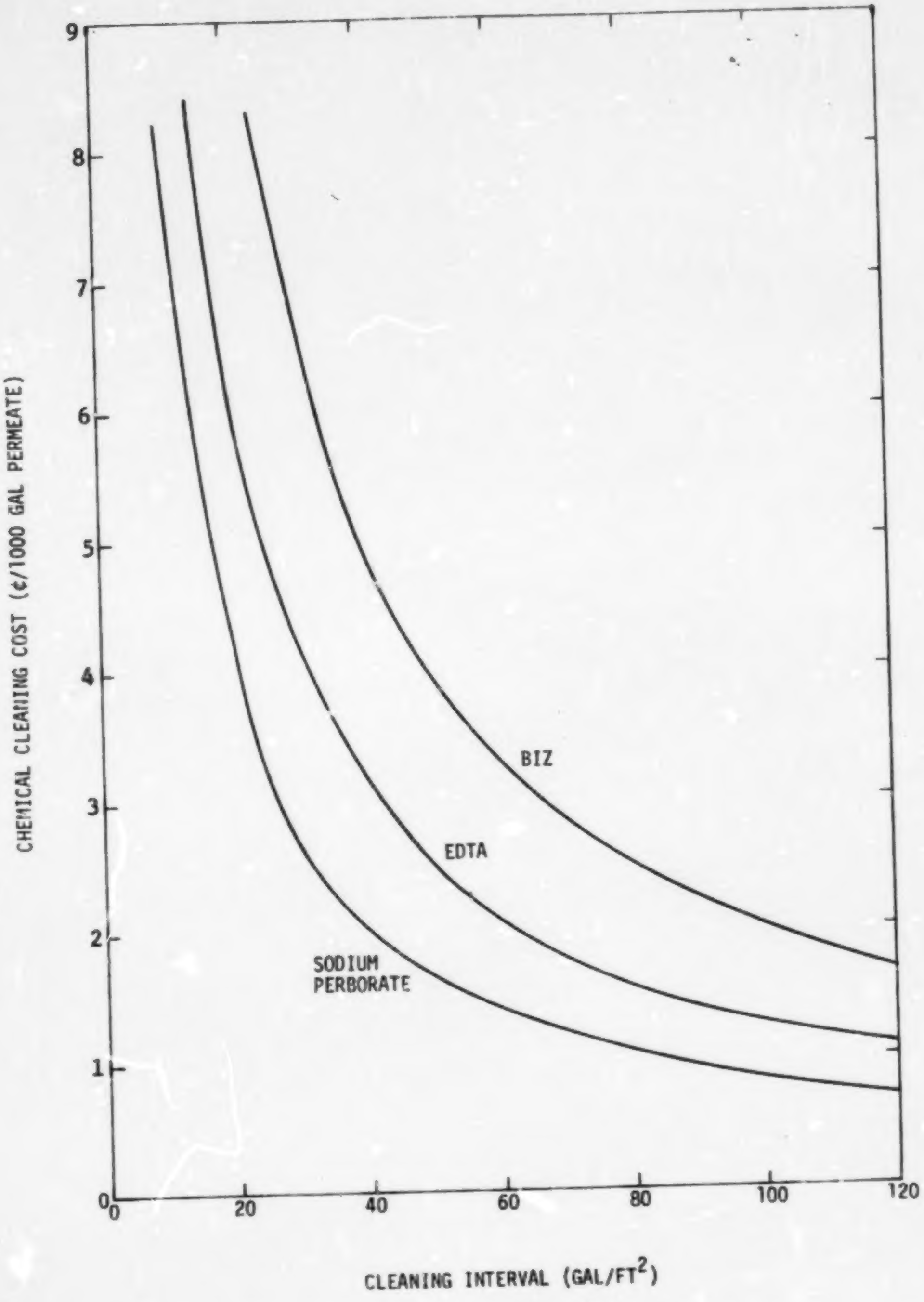


Fig. 35. Cost of chemicals for cleaning

TABLE 14
COSTS OF CLEANING SOLUTIONS

Basic Chemicals (quantity prices)	Cost ($/lb)
Sodium perborate ($NaBO_3 \cdot 4\ H_2O$)	$0.1675
EDTA (tetra sodium salt)	0.55
BIZ enzyme detergent	0.48
Triton X non-ionic detergent	0.38
Carboxy methyl cellulose	0.44

Cleaning Solution	Cost ($/100 gal. solution)
1. 2% $NaBO_3 \cdot 4\ H_2O$ 0.15 Triton X-100 0.0015% carboxy methyl cellulose	3.28
2. 1% EDTA 0.15% Triton X-100 0.0015% carboxy methyl cellulose	5.07
3. 2% BIZ	8.02

Down-time is another factor to consider in the cost of chemical cleaning. It creates a need for increases in the capacity of the unit, the product water storage capacity, and the module replacement costs. A large unit would probably be cleaned in sections, so that some water would always be produced. It is assumed for this analysis that the cleaning is performed at times of low water demand and that increased product water storage capacity is either minimal or not required. Calculations are based on the following estimates of plant costs:

Unit Size (MGD)[a]	Price ($1000)	Incremental Operating Cost (¢/1000 gal. permeate)		
		Capital Recovery of Unit	Module Replacement	Total for These Factors
1	473	10.4	13.8	24.2
10	3663	8.0	11.0	19.0
100	27,500	6.0	11.0	17.0

(a) Million gallons per day

The operating cost is calculated on the basis of a 25-yr, 6% capital charge and a 3-yr module lifetime at 10 gfd.

At the 1-MGD level, costs of down-time for a 1-hr cleaning are as follows:

Cleaning Interval ($gal./ft^2$)	Permeate Flux (gfd)	Cost of Down-Time (¢/1000 gal.)
25	10	0.40
	20	0.80
50	10	0.20
	20	0.40
100	10	0.10
	20	0.20

These costs, which are conservative in light of the module lifetime flux assumption, would be 22% and 30% lower at the 10-MGD and 100-MGD levels, respectively. Down-time cost increases with permeate flux in this example; however, this cost would be greatly outweighed by the decreased initial cost of a high-flux unit.

The units at Pomona have been depressurized daily and flushed with tap water. It is assumed that on a large unit the depressurization and flushing could be done automatically with negligible down-time and operating labor.

For determining the cost of operational labor for cleaning, it is assumed that a 1-hr cleaning of a 100,000-gpd section requires 1 hr of labor (which is probably conservative) and that the labor cost is $10,000/yr. The following charges would be incurred:

Cleaning Interval ($gal./ft^2$)	Permeate Flux (gfd)	Labor Cost (¢/1000 gal.)
25	10	1.92
	20	3.84
50	10	0.96
	20	1.92
100	10	0.48
	20	0.96

The labor cost for cleaning a large plant is the principal unknown in this analysis. Operational data on a larger unit designed for continuous operation are needed to better estimate this cost.

Total costs of chemical cleaning for perborate are shown in Fig. 36. The cost increases with decreasing intervals between cleaning and with increasing permeate flux. Plant size (about 100,000 gpd) does not have a large effect on cleaning cost; the largest factor appears to be the chemical costs. Cleaning costs are small compared with their very beneficial effect on the water flux.

Pretreatment or Additive Cost

When the cleaning costs become excessive, it is more economical to employ pretreatment measures. Effective pretreatment lengthens the interval between cleanings and thus reduces the cleaning cost. Representative costs of common pretreatment methods are listed below:(16)

Processes (Assuming a Secondary Effluent Feed)	Treatment Cost (¢/1000 gal.) at 75% Water Recovery		
	1 MGD	10 MGD	100 MGD
Sand or graded media filtration (4 gpm/ft^2)	8.3	3.7	1.6
Microscreening or roughing filter	1.6	1.3	1.2
Granular carbon adsorption	41.3	13.6	9.3

These costs include operating, maintenance, and debt service (4.5%, 25 yr) as of March 1969. Organic removal by activated carbon as a pretreatment on secondary effluent feed does not appear to be as economical as cleaning even at the 100-MGD level.

Additives are often employed to control membrane fouling. One example is the use of sodium hexametaphosphate as a threshold inhibitor to prevent scaling by calcium sulphate or calcium carbonate. An additive has not yet been found to prevent organic fouling. Nevertheless, it is still important to compare additive and cleaning costs to determine the economic limits of

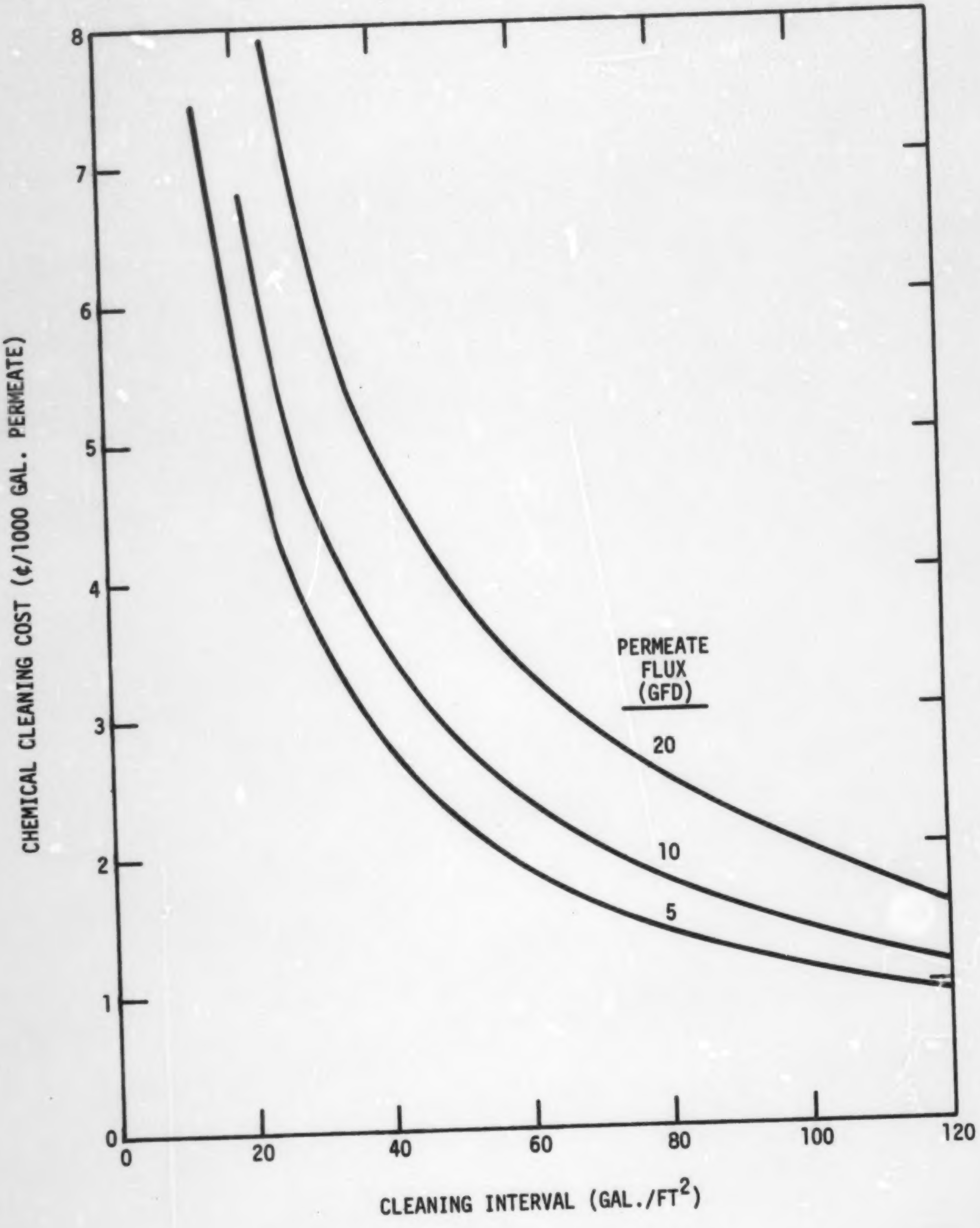


Fig. 36. Total chemical cleaning costs

chemical addition. Figure 37 indicates the cost of chemical addition versus the additive cost and the amount injected. A comparison of this graph with Fig. 36 indicates the desirability, from an economic standpoint, of a low-cost fouling-prevention additive at low injection levels.

REVERSE OSMOSIS TREATMENT OF MUNICIPAL WASTEWATER

Results of the field experiments have shown the technical feasibility of spiral-wound reverse osmosis unit operation on primary and secondary effluents with minimal pretreatment and chemical cleaning. The following rough analysis was made in order to compare the economics of the various treatment combinations.

Representative costs of primary, activated-sludge, sand filtration, and other tertiary processes are shown in Table 15. All of these total treatment costs with the exception of physicochemical were compiled by Smith and McMichael.(16) The totals include operation, maintenance, and capital recovery (6%, 25 yr) as of January 1970. Physicochemical treatment cost estimates were obtained from W. J. Weber, Jr.(18)

Representative costs of spiral-wound reverse osmosis systems are indicated in Table 16. These costs are based upon 85% water recovery, current capital costs (6%, 25 yr), and a permeate flux of 10 gfd. They do not include chemical cleaning, because this cost is dependent upon the feedwater and degree of pretreatment. For comparison purposes, total operating costs have been computed for membrane lifetimes of 3 yr and 2 yr. The operating membrane life on brackish water is greater than 3 yr, but tests lasting 3 yr have not yet been conducted on municipal effluents. However, life tests under this program have not indicated any loss of membrane salt rejection in the longer-term runs (4940 hr maximum).

The initial cost of a reverse osmosis plant includes pumps, membrane modules, pH controllers, chlorinators, chemical feed pumps, booster pumps, and a product water decarbonator and post-treatment system. A large portion of this initial cost is tied up in the membrane modules, which is a prepaid operating expense. The portion of the initial cost represented by membrane modules varies from

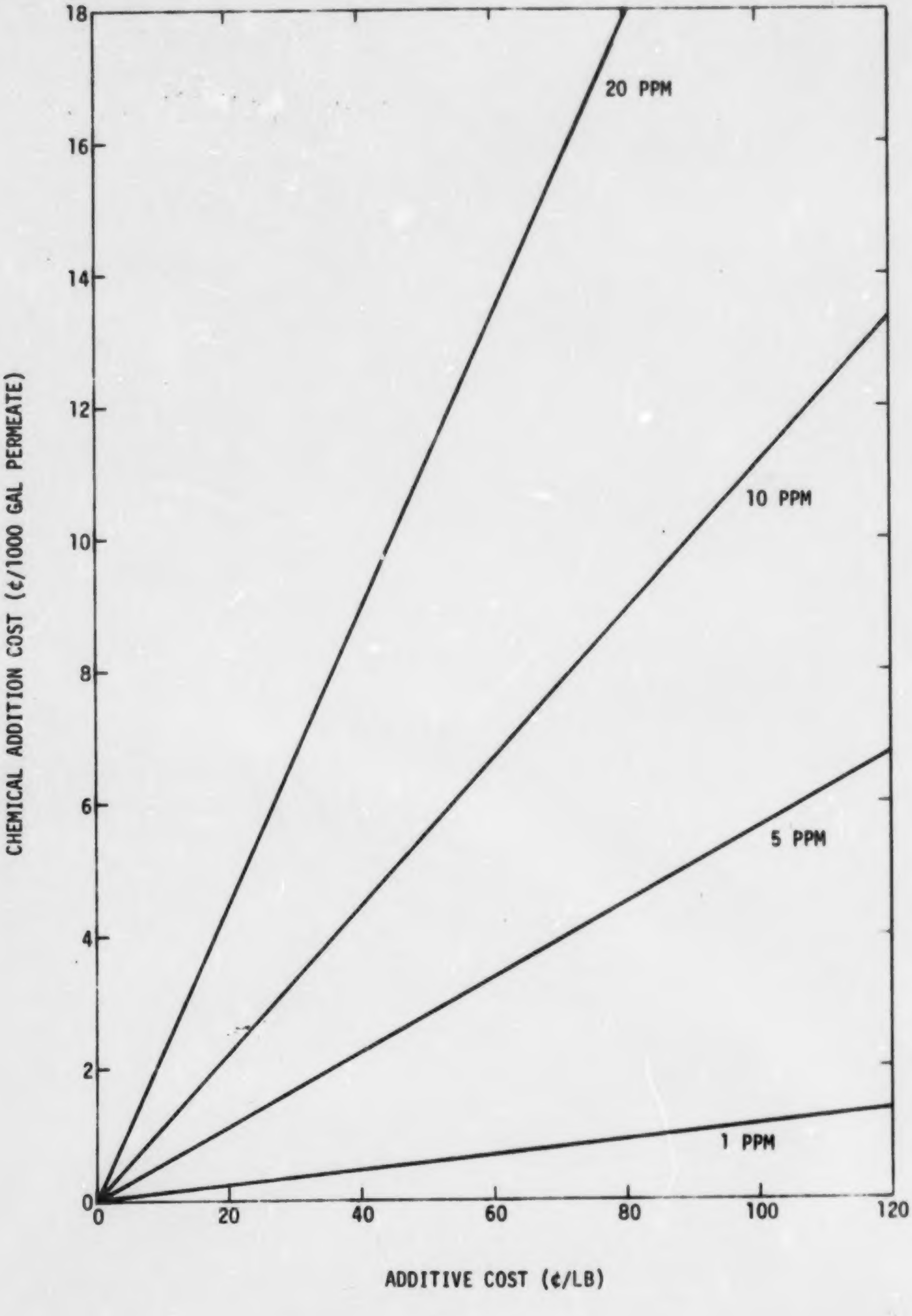


Fig. 37. Feed additive costs

TABLE 15
REPRESENTATIVE COSTS OF MUNICIPAL WASTE TREATMENT PROCESSES

Process	Treatment Cost (¢/1000 gal.)		
	1 MGD	10 MGD	100 MGD
Primary treatment (includes sludge disposal)	13.7	7.7	4.4
Activated sludge (includes primary & sludge disposal)	23.3	13.5	8.2
Dual media filtration of secondary effluent	6.8	3.0	1.4
Microscreening of secondary effluent	1.4	1.1	0.9
Activated-carbon treatment of secondary effluent	32.3	10.8	7.2
Two-stage lime clarification of secondary effluent (with recalcination)	20.9	8.4	5.0
Separate denitrification	11.5	4.0	2.0
Chemical clarification of raw sewage ($FeCl_3$)	19.3	13.3	10.0
Activated-carbon treatment of chemically clarified raw sewage	25.0	8.4	5.6
Chlorination to 8 mg/l	2.3	0.9	0.3

31% for 1 MGD capacity to 42% for 100 MGD capacity. Membrane replacement costs were based on setting up a sinking fund at 5% interest that would generate enough money at the end of each membrane lifetime to purchase an additional set of modules. Power costs were based upon a pump discharge pressure of 500 psi and a combined pump and motor efficiency of 65%. Chemical costs were based upon a 75% feed alkalinity reduction from a level of 150 mg/l (as $CaCO_3$) using sulfuric acid. It was assumed that 66° Baumé H_2SO_4 could be purchased at $30/ton. To inhibit calcium sulfate precipitation, sodium hexametaphosphate (16¢/lb) was presumed to be added at 5 mg/l.

Operating and maintenance costs were based upon operating 330 days per year with a labor rate of $10,000 per year. Labor and material costs are as follows:

TABLE 16
REPRESENTATIVE COSTS OF SPIRAL-WOUND REVERSE OSMOSIS OPERATION
(85% Water Recovery)

Cost Component	Treatment Cost (¢/1000 gal.)		
	1 MGD	10 MGD	100 MGD
Capital recovery (6%, 25 yr)	10	7.8	5.8
Power (1¢/Kwh)	6.4	6.4	6.4
Chemicals	2.4	2.4	2.4
Operation and maintenance	5.4	1.8	0.6
Membrane replacement			
2-yr life	21.3	17.0	17.0
3-yr life	13.8	11.0	11.0
Total operating cost			
2-yr life	45.5	35.4	32.2
3-yr life	38.0	29.4	26.2
Capital cost (millions of dollars)	0.47	3.66	27.5

	Unit Size		
	1 MGD	10 MGD	100 MGD
Labor (1000 $)	10	30	50
Material (1000 $)	6.2	30	150
Total (1000 $)	16.2	60	200
¢/1000 gal.	5.4	1.8	0.6

Cleaning costs varied with the type of feed and pretreatment. Table 17 indicates these expenses for the streams investigated in the field tests. In general, carbon treatment lowered the cleaning cost. However, the reduction was not enough to pay for the carbon treatment.

TABLE 17
ESTIMATED CLEANING COSTS OF SPIRAL-WOUND REVERSE OSMOSIS OPERATION ON MUNICIPAL EFFLUENTS[a]

Feed and Pretreatment	Interval Between Cleanings (gal/ft^2)	Cleaning Cost (¢/1000 gal.)
Secondary effluent, carbon treated	75	1.8
Secondary effluent, sand filtered	40	3.5
Primary effluent, chemically clarified and sand filtered	25	5.6 6.9 (EDTA)
Primary effluent, chemically clarified and carbon treated	40	3.5 4.2 (EDTA)

[a] Basis: Sodium perborate chemical cleaning agent, 10 gfd permeate flux. The effect of plant size above 1 MGD was neglected.

Table 18 compares total operating cost estimates of several treatment combinations that will significantly reduce contaminant levels in raw municipal wastewater. Ion exchange costs were obtained from the Los Angeles County Sanitation Districts.(19) Other treatment costs were obtained from Tables 15, 16, and 17. Brine disposal was not included in any of the treatment combinations.

Combination 1 is conventional secondary treatment, where BOD_5 removal averages 85%. Combination 2 adds activated-carbon treatment for higher organic removal. This water may be suitable for general reuse by blending with reverse osmosis or ion exchange product water and disinfection. Combination 3 is a tertiary process scheme designed to remove COD, phosphate, and nitrate from wastewater. With disinfection, effluent from this process may be suitable for reuse by blending with desalted water for TDS adjustment.

TABLE 18

ESTIMATED TOTAL OPERATING COSTS OF SEVERAL TREATMENT COMBINATIONS

Combination of Treatment Processes	Treatment Cost (¢/1000 gal.)			Estimated Total Contaminant Removal (%)			
	1 MGD	10 MGD	100 MGD	COD* or BOD_5**	Phosphorous	Nitrogen	TDS
1. Primary + activated sludge (including sludge disposal)	23.3	13.5	8.2	85**	--	--	--
2. Primary + activated sludge + activated carbon	55.6	24.3	15.4	97*	--	--	--
3. Primary + activated sludge + activated carbon + lime treatment + separate nitrification + chlorination	90.3	37.6	22.7	97*	98	85	--
4. Primary + activated sludge + activated carbon + ion exchange + chlorination		47.2 (700 mg/1) 60.2 (1000 mg/1) 73.9 (1500 mg/1)		98*	99	76 (NH_3-N) 86 (NO_3-N)	86
5. Primary + activated sludge + dual media filtration + reverse osmosis	71.6	49.4	39.3	99+*	99.7+	95 (NH_3-N) 75 (NO_3-N)	95
6. Primary + activated sludge + activated carbon + reverse osmosis	95.4	55.5	43.4	99+*	99.7+	95 (NH_3-N) 75 (NO_3-N)	95
7. Chemically clarified raw sewage + activated carbon + reverse osmosis (product aeration)	86.5	55.3	46.0	95+*	99.7+	90 (NH_3-N) 75 (NO_3-N)	95
8. Chemically clarified raw sewage + dual media filtration + reverse osmosis (product aeration)	64.2	49.6	43.1	95+*	99.7+	90 (NH_3-N) 75 (NO_3-N)	95

Combination 4 adds dissolved solids removal by ion exchange to Combination 2. With disinfection, this water may be blended with water from Combination 2 or 3 for general reuse. In Combinations 5 through 8, reverse osmosis is coupled to primary and secondary effluents with some additional pretreatment. Water from these schemes could be blended with effluent from Combination 2 or 3 for general reuse. Because the reverse osmosis membrane is a barrier to turbidity, bacteria, and viruses, the amount of chlorine used for disinfection is minimal because of its greater effectiveness. A 3-yr membrane lifetime was assumed.

Comparing the different combinations reveals that reverse osmosis and ion exchange costs are very close at a feed TDS of 700 mg/l. If one computes the blended water cost with carbon-treated effluent to produce 500 mg/l TDS water, the costs are essentially equal. As the salinity of the feed increases, reverse osmosis becomes the more economical process. Another advantage of reverse osmosis is that it does not significantly increase the TDS budget. Regenerant chemicals used in ion exchange do represent a significant dissolved solids addition.

A comparison with electrodialysis must be performed on a blended water basis because of the low removal of TDS. At the 10-MGD level, the total operating cost of electrodialysis operating on carbon-treated secondary effluent on a feed of 550 mg/l with 35% removal is 18.2¢/1000 gal.(20) The total treatment cost would be 42.5¢/1000 gal. Starting with the same feed, this product water can be obtained by blending activated-carbon effluent (Combination 2) with reverse osmosis product water (Combination 5). The blended water cost would be 33¢/1000 gal.

At the 1-MGD level, total treatment costs of the reverse osmosis combinations are lower than the costs of the conventional tertiary treatment scheme (Combination 3). This indicates that reverse osmosis may be a preferred method of tertiary treatment in smaller plants. General reuse of the product water would be an additional advantage.

In conclusion, this rough economic comparison demonstrates that reverse osmosis treatment costs are favorable. From a cost standpoint, a filtered activated-sludge effluent and filtered, chemically clarified raw sewage appear to be the best reverse osmosis feed streams. The reverse osmosis process merits serious consideration in a planned water supply and waste management program.

SECTION VII

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SECTION VIII

PUBLICATIONS AND PATENTS

The following publications have been derived in part from this study:

1. Nusbaum, I., Cruver, J. E., and Sleigh, J. H., "Reverse Osmosis - New Solutions and New Problems," Chemical Engineering Progress, 68, No. 1, pp 69-70 (1972).

2. Nusbaum, I., Cruver, J. E., and Kremen, S. S., "Recent Progress in Reverse Osmosis Treatment of Municipal Wastewater," Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, to be published (presented at the A.S.C.E. National Water Resources Engineering Meeting, Atlanta, Georgia, January 1972).

SECTION IX

APPENDICES

APPENDIX A
INORGANIC MEMBRANE DEPOSIT ANALYSIS TECHNIQUE

1. Remove deposit from membrane. If an organic analysis is required, place a suitable portion in a weighed vial and store immediately in the refrigerator.

2. Weigh a second sample on a watch-glass and dry at 105°C. Determine the loss of weight on drying. Grind the dried material in a mortar.

3. Weigh duplicates of the dried material in platinum crucibles and ignite at 600°C. Calculate the loss of weight on ignition. This loss will include organic material and water of hydration.

4. Perform the following analysis on duplicate samples of the dried material. (See Fig. 38.)

5. Weigh out approximately 0.5 g to the fourth decimal place in a 250-ml beaker. Let weight = W_1.

Carbonate

6. Pipette 25 ml of 0.2000 N HCl onto the sample. Stir with a magnetic stirrer for a few minutes.

$$CaCO_3 + 2HCl \rightarrow CO_2 + CaCl_2 + H_2O$$

7. Back-titrate the excess HCl with 0.2000 N NaOH to pH 3.2 using the pH meter. Let volume = V_1.

$$\%\ CO_3 = \frac{0.6}{W_1}(25 - V_1)$$

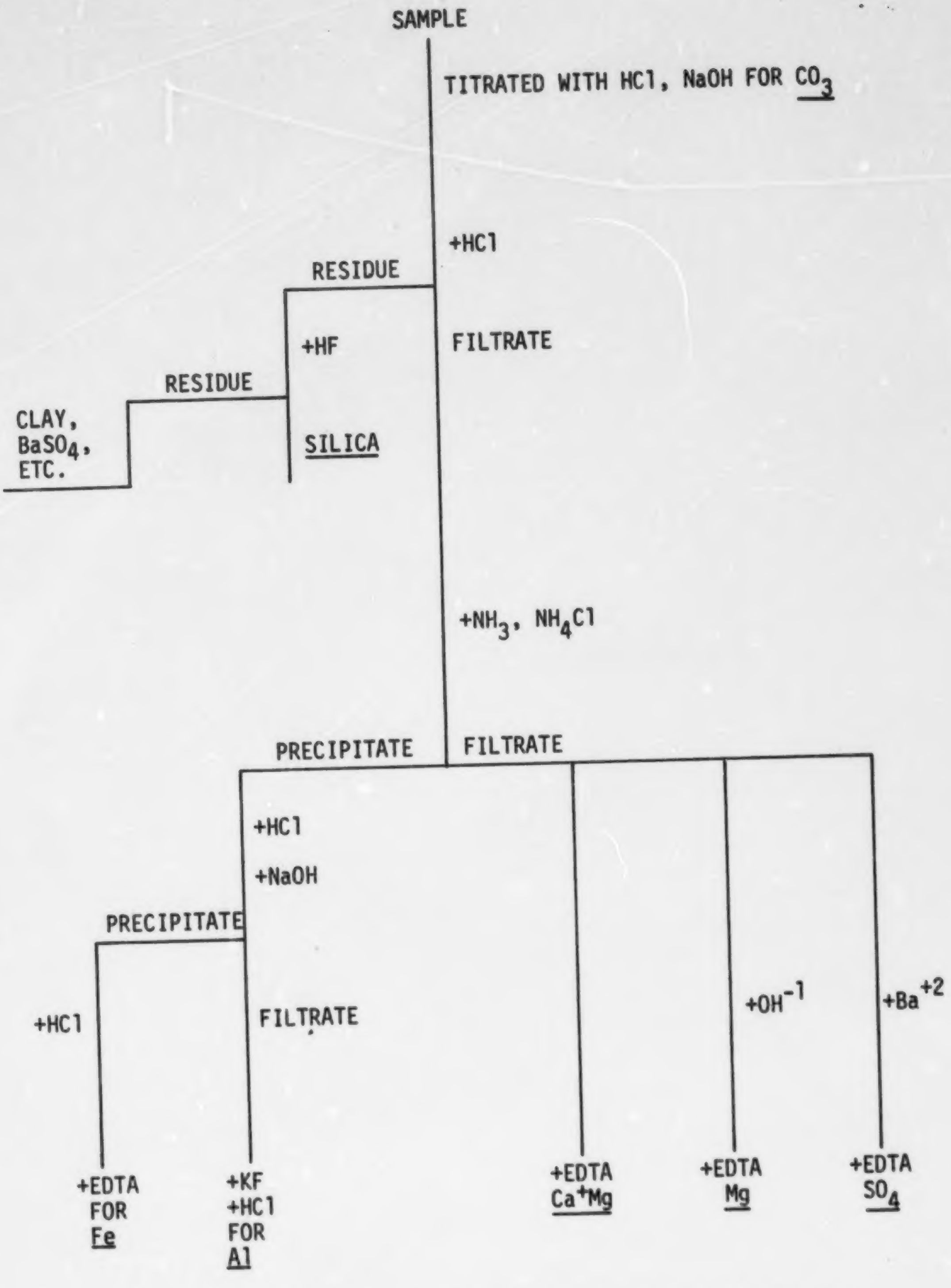
SAMPLE
TITRATED WITH HCl, NaOH FOR CO3
+HCl
RESIDUE
+HF
FILTRATE
RESIDUE
CLAY, BaSO4, ETC.
SILICA
+NH3, NH4Cl
PRECIPITATE
FILTRATE
+HCl
+NaOH
PRECIPITATE
+HCl
FILTRATE
+OH-1
+Ba+2
+EDTA FOR Fe
+KF +HCl FOR Al
+EDTA Ca+Mg
+EDTA Mg
+EDTA SO4

Fig. 38. Inorganic membrane deposit analysis technique

8. Dilute the mixture to about 100 ml and add 5 ml HCl and 3 drops HNO_3. Heat to boiling, and then stir with magnetic stirrer for 1 hr. Filter through No. 41 paper. Wash thoroughly with cold, then hot, water. Use a policeman if necessary.

Silica

9. Place the filter from (8) in a tared platinum crucible, char over a burner, moisten with water, add 2 drops H_2SO_4, fume, and ignite for 1 hr at 1000°C in a muffle furnace. Cool in a dessicator and weigh (W_2).

10. Add 3 ml 48% HF. Evaporate, add 2 drops H_2SO_4, fume, ignite, and weigh again (W_3).

$$\% \ SiO_2 = \frac{(W_2 - W_3)\ 100}{W_1}$$

Residue

11. The residue, W_3, would include "insoluble" iron and aluminum contributed by clay and also barium sulfate.

12. To the filtrate obtained in (8) add about 25 ml of ammonium chloride solution (Reagent 1; reagents are listed at the end of this appendix) and 1 drop methyl red (0.2% alcoholic solution) and heat to boiling. Add dilute (1:1) ammonium hydroxide drop by drop until the color just changes to yellow. Boil for 2 or 3 min with constant stirring and filter at once on No. 41 paper. Wash with hot 2% NH_4Cl solution.(17)

$$Al^{+3} + 3OH^{-1} \rightarrow Al(OH)_3 \downarrow$$

$$Fe^{+3} + 3OH^{-1} \rightarrow Fe(OH)_3 \downarrow$$

13. Dilute filtrate and wash waters to 250 ml.

14. Pour 50 ml warm 10% HCl through the filter obtained in (12), add 23 ml of 10% NaOH, then nearly neutralize. Pour with constant stirring into 50 ml of hot, freshly prepared 10% NaOH. Boil 2 or 3 min, let settle 1 hr, and filter through No. 41 paper. Wash with 2% NaOH.(18)

$$Fe^{+3} + 3OH^{-1} \rightarrow Fe(OH)_3 \downarrow$$

$$Al^{+3} + 4OH^{-1} \rightarrow Al(OH)_4^{-1}$$

Iron

15. Pour 50 ml warm 10% HCl through the filter obtained in (14), dilute to 100 ml, and take a 20-ml aliquot. Dilute this to 100 ml, add 3 ml of 10% NaOH, and then neutralize to pH 2.5. Add 2 ml of 2% Tiron, warm to 40° to 50°C, and titrate with 0.02500M EDTA until the green color disappears.(19) Let volume = V_2.

Where Y = EDTA anion,

$$Fe^{+3} + H_2Y^{-2} \rightarrow FeY^{-1} + 2H^{+}$$

$$\% \; Fe = \frac{0.698V_2}{W_1}$$

Aluminum

16. Cautiously add 40 ml of 10% HCl to the filtrate obtained in (14). Then neutralize by the drop-by-drop addition of HCl to pH 11. Wash down the electrodes and beaker with water and dilute to 300 to 350 ml. Adjust the pH to 10 with 0.2 N HCl. Then add 40 ml of 30% KF and titrate to pH 10 with 0.2000 N HCl.(20) Let volume = V_3.

$$Al(OH)_3 + 3F^{-1} \rightarrow AlF_3 + 3OH^{-1}$$

$$\% \text{ Al} = \frac{0.180V_3}{W_1}$$

Calcium

17. Pipette a 25 ml aliquot of the filtrate obtained in (12), adjust pH to >10.5 with 10% NaOH, and add 0.2 g of Murexide indicator (Reagent 2). Titrate against 0.02500M EDTA solution until the pink color changes to purple.(21) Let this volume = V_4.

Where Y = EDTA anion,

$$Ca^{+2} + H_2Y^{-2} \rightarrow CaY^{-2} + 2H^+$$

$$\% \text{ Ca} = \frac{1.02V_4}{W_1}$$

Magnesium

18. Pipette a second 25 ml aliquot, add 3 ml of 0.02500M $MgCl_2$ solution and 10 ml of ammonia buffer (Reagent 3). The pH should be >10. Add 5 drops of Eriochrome Black T (Reagent 4) and titrate with 0.02500M EDTA until the color changes from wine-red to pale blue.(22) Let this volume = V_5. The calcium forms a less stable complex with the dye than does the magnesium, so the overall titration may be represented as follows (In = indicator anion):

$$Ca^{+2} + H_2Y^{-2} \rightarrow CaY^{-2} + 2H^+$$

$$\underset{\text{wine-red}}{MgIn^{-1}} + H_2Y^{-2} \rightarrow MgY^{-2} + \underset{\text{pale blue}}{HIn^{-2}} + H^+$$

$$\% \text{ Mg} = \frac{0.608}{W_1}(V_5 - V_4 - 3)$$

Sulfate

19. Pipette a 25-ml aliquot of the filtrate obtained in (12), boil, and add 25 ml of 0.02500M $BaCl_2$ solution. Cool, and add 3 ml of 0.02500M $MgCl_2$ solution and 10 ml of buffer (Reagent 3). The pH should be >10. Add 5 drops of Eriochrome Black T (Reagent 4) and titrate with 0.02500M EDTA solution until the color changes from wine-red to pale blue.(23) Let volume = V_6.

$$Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4 \downarrow$$

$$Ca^{+2} + Mg^{+2} + Ba^{+2} + 3H_2Y^{-2} \rightarrow CaY^{-2} + MgY^{-2} + BaY^{-2}$$

$$\% \ SO_4 = \frac{2.40}{W_1} (25 - V_6 - V_5)$$

REAGENTS

Reagent No.	
1	Dilute 200 g NH_4Cl and 120 ml NH_4OH to 1 liter.
2	Grind together 0.20 g of Murexide and 100 g NaCl and mix thoroughly.
3	Dilute 68 g NH_4Cl and 570 ml NH_4OH to 1 liter.
4	Dissolve 1 g Eriochrome Black T in 30 ml of 0.18% Na_2CO_3 solution. Dilute to 100 ml.

APPENDIX B

PHYSICOCHEMICAL TREATMENT DATA

Interest in physicochemical treatment of primary effluent or raw sewage has recently increased as the result of several published investigations.(28) A physicochemical treatment unit was constructed under this program to furnish feed streams for reverse osmosis unit field tests. This treatment system was composed of an upflow clarifier, which also served as a reacting chamber for flocculation, two pressurized sand filters, and a granular carbon adsorber.

The upflow clarifier had a square cross section, 6 ft x 6 ft, and was 8 ft high. This design, by California Filter Company, was called a "Reactifier." It incorporated a chevron baffle located about 3 ft above the bottom which separated the tank into a reacting section and a clarifying section. Feed entered the reacting section at the apex of the chevron and flowed into the clarification section around the chevron's outer edges. Two 4-in. pipes at the bottom corners of the tank drew off the sludge at regular intervals. The manufacturer rated this piece of equipment for 20 gpm overflow. However, with the high suspended and colloidal solids content of the primary effluent, the maximum overflow achieved during testing was 15 gpm.

Aluminum sulfate and ferric chloride were tested as possible coagulants, and several polymers were evaluated as coagulant aids. Jar tests indicated that both compounds could be used to reduce the turbidity to less than 20 JTU. The primary effluent turbidity fluctuated widely throughout each day. For this reason, it was necessary to use 90 to 105 ppm $FeCl_3$ or 300 ppm aluminum sulfate.

Coagulant aids were effective in increasing the clarifier overflow without a turbidity increase. Concentration was not as critical as with the inorganic coagulants. Nonionic polymers appeared to function better with ferric chloride and anionics performed better with aluminum sulfate.

Ferric chloride and Magnifloc 985-N (American Cyanamid) were selected for clarifier operation. Ferric chloride could be added at lower concentration than aluminum, and the ferric hydroxide floc was not destabilized as the pH was lowered for reverse osmosis unit operation. On the other hand, aluminum hydrate decreases in solubility as the pH is lowered from 7 to 5.5. The dosages of $FeCl_3$ and polymer required for a 15 gal./min clarifier overflow were 90 mg/l and 1 mg/l, respectively.

After leaving the clarifier, the flow was divided into two streams. Each passed through a sand filter, and one of the streams passed through a down-flow packed activated-carbon adsorber. The pressurized sand filters were standard packaged designs by L.A. Water Conditioning Company. Each was 30 in. in diameter and had 7 ft^3 of sand. They were operated in the range of 1.5 to 3.0 $gal./ft^2$ of bed area. The carbon filter was also a standard L.A. Water Conditioning design. It was 4 ft in diameter with a 5-ft bed height. Calgon Filtersorb No. 400, 12 x 40 mesh activated carbon was used as an adsorbant.

Table 19 shows typical performance data for the clarifier plus sand filter. Average reductions in total COD and turbidity were 60% and 94%, respectively. Phosphate removal was also very good, and the alkalinity was reduced about one-half. Subsequent treatment with activated carbon of one of the sand filter effluents further reduced the COD to 20 to 22 mg/l, a total reduction of about 85%.

TABLE 19
PHYSICOCHEMICAL TREATMENT DATA
(Units are mg/l unless otherwise specified.)

Species	January 5, 1971		March 18, 1971	
	Primary Effluent	Sand-Filtered Clarified Primary Effluent	Primary Effluent	Sand-Filtered Clarified Primary Effluent
Sodium	108	91.0	140	100
Potassium	9.3	9.0	15.5	14.0
Ammonia nitrogen	23.0	24.5	30.0	30.6
Calcium	53.0	46.0	71.0	66
Magnesium	15.1	15.1	10.8	9.6
Chloride	182	234	181	197
Nitrate nitrogen	1.6	0.6	4.6	1.7
Sulfate	56.4	41.4	62.0	63.6
Orthophosphate	0.42	<0.2	5.13	0.22
Total COD	130	52.3	138.9	54.2
Dissolved COD	62.1	25.0	61.4	48.2
Total alkalinity	256	122	224	132
Turbidity (JTU)	37	2.17	49	2.43
pH (pH units)	7.8	6.9	7.6	6.8
TDS	670	657	748	638
Conductivity (μmho)	1190	1170	1270	1120